

A TEXT BOOK ON HEAT

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A TEXT BOOK ON HEAT

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PREFACE

THIS book has been written to satisfy the needs of students reading for University Entrance Scholarships and the various Higher School Certificate and University Intermediate examinations. It is also hoped that it will be sufficient for those readers who do not intend to carry the study of this subject beyond the Pass Degree stage.

While it is now generally accepted that Science should form a part of the general education of every citizen, there is still a feeling that its claim to recognition lies rather in its "utility" than in its cultural value. I have written this book in the hope of showing that the study of natural knowledge is as truly cultural as that of literature or art. From this point of view the fundamental aim of the teacher of Science should be to try to instil into his pupils some interest in the phenomena of Nature for their own sake, to develop the spirit of enquiry, to train them in reliable observation and the judicious summing up of evidence, to foster the imagination needed to frame hypotheses to explain his observations, and lastly to develop some little appreciation of the beauty of the rational scheme which has been created by the mind of man to explain the phenomena of Nature. I have tried, therefore, not only to describe the investigations which have been made and the theories which have been put forward to account for them in the realm of Heat, but also to bring out the reason for the various experiments. An attempt has been made to show that every piece of work, experimental or theoretical,

was undertaken to solve some problem of particular interest. For example, before describing the experiments of Amagat, Regnault, and others on Boyle's law at high pressures, it is suggested that this work was undertaken to see if the so-called "permanent gases" showed deviations from the law similar to those of the liquefiable gases, in which case it was probable that they themselves were not "permanent." The historical method of treating the subject has therefore been adopted, as this seemed to be the most appropriate way of illustrating that Science is a living subject, and that the scientist carries out his work to solve some problem which interests him. He expresses himself in his work no less than the artist, for example, and is as indifferent to material reward or popular recognition. Nevertheless, the historical method has not been slavishly adhered to, and some of the older forms of apparatus, such as Bunsen's ice calorimeter, have been omitted, if they have now been replaced by other, more accurate, methods. In the same way, recent methods for the standard determinations, such as specific heat, latent heat, and the compressibility of gases, have been added when they seemed sufficiently important to warrant inclusion in a book of this standard. An attempt has also been made to encourage the critical faculty of the reader by not only describing the apparatus and experimental procedure, but also by pointing out the reasons for the form the apparatus actually took and by drawing attention to its defects no less than to its good points. Finally, I have not hesitated to point out the inadequacy of the classical theories in the case of specific heats and radiation in order to instil into the reader that any one theory is only an approximation to the truth and is liable to failure, modification, and perhaps rejection in the light of new facts.

A considerable variety of questions has been set at the end of each chapter and includes routine descriptive questions, numerical examples, and essay questions. Some of these have been composed by the author and the

others are reproduced from various examination papers by kind permission of the Cambridge University Press, the Northern Universities Joint Matriculation Board, the University of London, and the Examining Boards to the two principal Groups of Oxford Colleges. The source of each question so reproduced is printed in brackets after it.

It is hardly necessary to acknowledge my indebtedness to the standard works on the subject such as Preston's *Heat*, Roberts' *Heat and Thermodynamics*, and Maxwell's *Theory of Heat*. I should also like to express my sincere thanks to Mr J. A. Ratchiffe, M.A., Fellow of Sidney Sussex College and University Lecturer in Physics at the Cavendish Laboratory, Cambridge, for his kindness in reading the manuscript and for his valuable criticisms and suggestions. I should also like to thank my colleague, Mr A. E. E. McKenzie, M.A., who has read the proofs and made a number of helpful suggestions.

REPTON SCHOOL, May, 1933.

The sources of the questions are indicated as follows.

<i>Camb Schol</i>	Entrance Scholarships at Cambridge Colleges
<i>Oxford Schol</i>	Entrance Scholarships at Oxford Colleges
<i>O. and C.</i>	Oxford and Cambridge Schools Examination Board Higher Certificate
<i>N U J B</i>	Northern Universities Joint Matriculation Board Higher Certificate
<i>Lond B Sc</i>	London University Pass B Sc Examination.
<i>Tripes, Part I</i>	Part I of the Natural Sciences Tripos, Cambridge University

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INTRODUCTION

SCIENCE may be defined as "the promotion of natural knowledge," "the pursuit of truth," or "the systematic investigation of the physical world," and its claim to be regarded as such is based largely on the method by which it searches for knowledge. The first and fundamental step is to ascertain the *facts* in connection with the problem under investigation by an appeal to experience, that is, by experimental investigation, for Science recognises no authority other than Nature. The next step is to *classify the facts* in order that their significance may be better appreciated, this involves ideally their expression in the form of a mathematical equation. The third and essential step is the formulation of a *theory* to explain the facts, this being the really outstanding part of the work, because Science is emphatically not a catalogue of facts but an attempt to fit them into a rational scheme. Finally it is demanded of a theory that it shall be capable of experimental verification and *shall lead to a search for new facts*, and so the journey is continued ever onwards into new realms of knowledge. The characteristic feature of this method is that it is constantly in touch with experimental fact and that is why Science can justly claim to be the pursuit of truth.

It is the aim of this book to exemplify the above principles in the case of Heat, and so the first seven chapters are devoted to an account of the appropriate experimental facts. The most fundamental conception in connection

with the science of Heat is that of temperature, the temperature of a body is simply how hot it is, or its degree of hotness. It is a measure of a certain physical condition of the body and is perceived primarily by the sense of touch. If we feel that of two objects A is hotter than B, then in scientific language the temperature of A is greater than that of B. Let us suppose that we raise the temperature of B till it is the same as that of A by putting a bunsen burner under it, what causes the change in temperature? It is both rational and in accordance with experiment to assume that the bunsen gives something to B which causes rise in temperature, we call this "something" *heat*, and it is unnecessary to postulate anything as to its nature. It is merely the *cause* of the observed *effect*—rise in temperature.

Having established clear and concise definitions of the two fundamental notions, temperature and heat, the accurate measurement of temperature is next considered, to be followed by an account of various determinations concerning quantity of heat, such as the specific heat of solids, liquids, and gases. Two of the commonest effects of heat are expansion and change of state and they are accordingly treated in the next four chapters of the book. This account of the experimental facts is concluded by a description of the properties of vapours and we are now in a position to consider the theories of heat. An account of the caloric theory and the evidence which led to its downfall serves to introduce the view now universally accepted that heat is a form of energy and a description of the experimental evidence in its favour is given. It is natural to enquire now as to what sort of energy heat may be, and the answer to this question is found in an attempt to explain the above facts on the assumption that heat is the energy of motion of the molecules of a body. The kinetic theory meets with its most striking success in the explanation of the ideal gas equation, but a number of assumptions, which are certainly untrue, are made to

simplify the calculations. This suggests that all actual gases deviate to a greater or less extent from the ideal gas, and an account is then given of the experiments of Andrews and Holborn, which verify the above supposition. This fuller investigation of the properties of gases leads us to consider on the one hand their liquefaction and on the other hand Van der Waals' equation, one of the most successful attempts to represent the behaviour of an actual gas by a mathematical equation. We have now firmly established the view that heat is a form of energy and we have already discovered the law governing the conversion of work into heat, the first law of thermodynamics. What law or laws govern the converse process? This problem is one of the greatest practical interest and its solution is to be found in the second law of thermodynamics, which has many theoretical applications, such as the "work scale of temperature". The book concludes with an account—largely experimental—of the three ways by which heat is transmitted, namely, convection, conduction, and radiation.

CHAPTER I

THE MEASUREMENT OF TEMPERATURE

1. Definition of a Scale of Temperature.—The first step in the science of heat is to learn how to measure temperature as a number, and further, to devise means of measuring it accurately. The sense of touch, which is the primitive way of measuring temperature, is useless for this purpose and is, moreover, very unreliable, as are all observations based on physiological sensations. For example, on a cold day a piece of iron will feel colder than a piece of wood; their temperatures are really equal, but the iron feels the colder because it is the better conductor, and so heat can more readily flow from the hand into the iron than into the wood. For the same reason on a hot day a piece of iron will feel the hotter. Physiological sensation, then, must be ruled out as far as possible, and the only exercise of it demanded in scientific work is the judgment of the coincidence of two lines, say the image of the cross-wire of a galvanometer lamp with the zero division on the scale, or the tangent to a mercury meniscus and the 98.4° F division of a clinical thermometer. It is necessary, then, to choose some property of matter which varies with hotness and on it to base a *scale of temperature*.

In order to construct a scale of temperature it is necessary to define the zero and to fix the size of the unit of temperature. This is done by choosing two temperatures, called the fixed points, which are constant and easily reproducible, and assigning two numerical values to them. The lower fixed point is the temperature at which pure ice melts at a pressure of 1 standard atmosphere and the upper fixed point is the temperature of steam from water boiling at a pressure of 1 standard atmosphere. The standard atmosphere is the pressure of a column of mercury

76 cm long at 0°C , at sea level, and 45° latitude. The temperature of steam, rather than that of boiling water itself, is chosen, as it has been found experimentally that the temperature of the boiling water varies even with the nature of the containing vessel. These fixed points are called 0° and 100° respectively on the Centigrade system of graduation, which is the only one used in scientific work.

We have so far defined two temperatures, we have now to construct a scale of temperature which will enable us to measure temperatures within and outside the range of the fixed points. To do this we take any property of matter which depends on hotness, such as the volume of a given mass of mercury, the pressure of a gas at constant volume, the volume of a gas at constant pressure, the resistance of a piece of platinum wire, the E M F of a thermo-couple, or the saturation vapour pressure of water. Let the magnitude of the property chosen be F_{ice} and F_{st} at the lower and upper fixed points respectively. Then if its magnitude is F at some other temperature, the numerical value, t_s , of that temperature is defined by the equation

$$\frac{t_s}{100} = \frac{F - F_{ice}}{F_{st} - F_{ice}}. \quad \dots \quad (1)$$

This defines any temperature at which the property chosen still persists. We shall now proceed to illustrate and amplify this general definition of a scale of temperature by applying it to a number of particular cases.

One of the first properties chosen was the expansion of matter when heated, and this led ultimately to the mercury

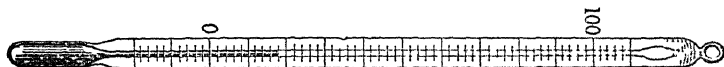


FIG. 1.

thermometer and the *mercury-in-glass* scale of temperature. The mercury thermometer (Fig. 1) consists essentially of a thick-walled capillary tube, which we will suppose to be uniform for the sake of argument, on the end of which is blown a bulb. The upper end of the capillary tube is

closed, the bulb and part of the stem being filled with mercury and the remainder with mercury vapour. The first stage in the calibration of the thermometer is to find the two fixed points. We now construct a scale of temperature by making use of the variation in the level of the mercury column with hotness. Let the length of the mercury column measured from any convenient point on the stem be l_{ice} and l_{st} at 0° C and 100° C respectively, and let its length be l_t when the thermometer is in some water. Then the temperature, t_m , of that water measured on the "mercury-in-glass scale" is given by the equation

$$\frac{t_m}{100} = \frac{l_t - l_{ice}}{l_{st} - l_{ice}}. \quad . \quad . \quad . \quad (2)$$

This equation defines a scale of temperature which covers all temperatures between the freezing and boiling-points of mercury. It is such that when the mercury is precisely half-way between its positions at 0° C and 100° C the body is at a temperature of 50° C; it is such that equal increases in length of the mercury column *define* equal increments of temperature. There is a tendency to think that this is naturally so because mercury really does expand uniformly with temperature, this argument is quite wrong and is indeed meaningless, because the word *really* presupposes the existence of a scale of temperature against which the expansion of the mercury is measured. But such a scale of temperature does not exist if we imagine ourselves to be the first persons who ever tried to invent one, and in any case it need not exist for our purpose. The point is that our scale of temperature is so *defined* as to make the length of the column increase uniformly with temperature.

It should be mentioned here that there are two other systems according to which a thermometer may be calibrated. On the Fahrenheit system the lower fixed point is marked 32 and the upper fixed point 212, and the space between them is divided into 180 equal parts. It is never used in scientific work although it is still in popular use in England; it seems to have been founded in the attempt to avoid negative temperatures, for 0° F was about the lowest temperature which could be reached at that time, using a freezing mixture of snow and salt. The Réaumur

system is used for domestic purposes on the Continent and has the two fixed points marked 0 and 80 respectively. It is a simple matter to convert temperatures from one system to another from first principles, and so no formula relating such temperatures is given.

The construction of a mercury thermometer and the determination of the fixed points are dealt with adequately in more elementary text-books and so they will not be referred to any further here.

2. Errors of the Mercury Thermometer.—The mercury thermometer can be made to read to 0.1°C or even 0.01°C if the various errors, which will now be enumerated, are allowed for.

(a) The bore of the capillary stem has been assumed constant for the sake of simplicity. It is impossible to obtain such a tube in practice, and so one as nearly uniform as possible is chosen and an appropriate correction is applied.

(b) The thermometer will give a lower reading in the vertical than in the horizontal position owing to the pressure of the mercury column increasing the size of the bulb and decreasing the volume of the mercury.

(c) If the bulb of the thermometer be subjected to an abnormally high external pressure, as for example when it is immersed in a dense liquid, this will decrease the size of the bulb and cause it to read too high. This effect can easily be demonstrated by holding the bulb of the thermometer between the thumb and finger until its reading is steady, on applying a small pressure the reading can be made to increase by as much as a degree, at once resuming its original value on releasing the pressure. A patient can easily give himself a "temperature" in this way by nipping the bulb of a clinical thermometer gently with his teeth, but he must be careful not to overdo it!

(d) It has been tacitly assumed that the whole of the mercury in the thermometer is at the temperature to be measured, but this is frequently not the case and causes the thermometer to read too low. This is called the *error of the exposed column*.

(e) Lastly there are errors in the 0°C . mark owing to the fact that glass is somewhat plastic, and so the bulb

of the thermometer does not return at once to its original size after it has been heated up

No account will be given of the way in which these errors are estimated and corrected for, since the current practice is to send a thermometer required for accurate work to the National Physical Laboratory to be tested. It is calibrated against a standard thermometer and is returned with a table which gives the true temperature corresponding to any reading on the thermometer, when used in a certain specified way (that is, when lying horizontally and with the stem only immersed up to the 10°C . mark, etc.)

The mercury thermometer is seldom used in accurate scientific work nowadays, having been replaced by the platinum resistance and thermo-electric thermometers. The reasons for this are

(a) Its limited range—mercury freezes at -39°C . and boils at 356°C ., whereas in the modern physics laboratory temperatures may be used from -272°C up to 3000°C !

(b) It can only read to an accuracy of 0.05°C over this range, and then only after making many troublesome corrections and being bound by limitations as to the method of use which cannot always be realised in practice

Nevertheless it has certain advantages which still make it useful in one or two cases where very accurate measurement is not required, for example, in weather observations and as a clinical thermometer in medical practice. Its advantages for this sort of purpose are

(a) It is easy to read, like all "pointer instruments"

(b) It is easy to use and carry about

3. Maximum and Minimum Thermometers.—Two of the measurements taken at every weather station are the maximum and minimum temperatures reached in the air during the twenty-four hours ending at 9 a.m. each day. These are both recorded by mercury thermometers which must have been standardised at the National Physical Laboratory and be used in a specified way, if the readings are to be accepted by the Meteorological Office. For example, they must be mounted almost horizontally with the bulb slightly lower than the top of the stem; thus, if the thermometer is standardised in this position, the

second error mentioned in Art 2 is eliminated. The thermometer will never be exposed to any abnormally high pressure, nor is there any error of the exposed column, so it is quite able to give readings accurate to 0.1°F , which is all that is required.

The maximum thermometer is calibrated from about 30°F to 130°F and the stem has a constriction at C (Fig 2). When the temperature rises, the enormous force of expansion—it will be of the order of tons—easily pushes

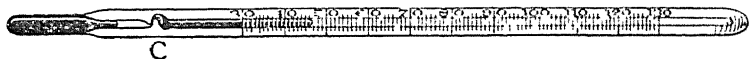


FIG 2

the mercury through the constriction, but as soon as it begins to fall there is only the weight of the thread of mercury above the constriction, perhaps a few grams, to force it down. This is quite insufficient, and so the thread of mercury continues to denote the maximum temperature of the day, which can be read at leisure. The thermometer is set by shaking the mercury through the constriction until it has joined that in the bulb once more.

A clinical thermometer works on precisely the same principle and is calibrated from 95°F . to 110°F . It is essential that, when the thermometer is removed from the patient's mouth, the mercury thread should remain fixed and not go down as it would do in an ordinary

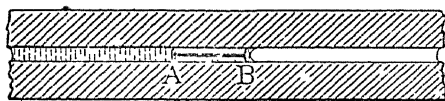


FIG 3

thermometer, otherwise the doctor would have to take the reading while the thermometer was still in the patient's mouth!

The minimum thermometer is filled with alcohol and contains a metal index AB (Fig 3). When the temperature is falling the *surface tension* of the alcohol drags the index down with it, but as soon as it begins to rise the *viscosity* of the alcohol cannot move the index, and so the end B denotes the minimum temperature reached during the

specified period. The instrument is set by tilting it until the index is again in contact with the alcohol meniscus and it is calibrated from about -20°F to 60°F . The reader is referred to the more elementary text-books for Six's maximum and minimum thermometer and other types.

4. The Constant Volume Gas Thermometer.—The preceding account of the mercury thermometer reveals certain distinct limitations, such as its restricted range and troublesome corrections. These defects are due in part to the variable behaviour of the glass, and this leads to a distrust of the mercury thermometer of a more fundamental nature. If two given mercury thermometers are made of different kinds of glass, will they give the same reading (except at 0°C and 100°C where they agree by definition) when placed in the same water-bath? It is found *by experiment* that they do not, and the theoretical reason for this disagreement will be discussed later. It is sufficient to emphasise here that the difference in readings is real and not due to experimental error. We are now confronted by a serious difficulty, namely, that no two mercury thermometers can be expected to agree. The trouble arises from the fact that the expansion of the glass is comparable with that of the mercury, and so it can be eliminated by choosing as the basis of our scale of temperature a substance whose expansion is large compared with that of glass. A gas at once suggests itself and can be used in two ways. Either the increase in volume at constant pressure, or the increase in pressure at constant volume may be chosen. Long experience has shown that *constant volume thermometers* are the easier to use and if anything give the more accurate results, and so the constant pressure thermometer will not receive any further consideration in this book.

Suppose that a given mass of a certain gas, say hydrogen, when kept at a constant volume exerts pressures p_{ice} , p_{st} , and p at the upper and lower fixed points and at the temperature of a water-bath respectively. Then the temperature, t_g , of that water-bath measured on the *constant volume hydrogen scale* is given by

$$\frac{t_g}{100} = \frac{p - p_{ice}}{p_{st} - p_{ice}} \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

adopted precisely the same way of defining the two temperature scales with regard to their respective properties and that in each case we have made use of the general equation (1). It can be seen from equation (3) that the constant volume hydrogen scale is so defined as to make the pressure of hydrogen at constant volume increase uniformly with temperature. This is so important that we shall demonstrate its truth by deriving equation (3) from the assumption that pressure varies uniformly with temperature.

If we assume a linear relation between pressure and temperature, the following equation is true.

$$p = p_{ice} (1 + \alpha t_g) \quad . \quad . \quad . \quad (4)$$

where α is a constant independent of temperature.

It must be emphasised that this equation is mathematically true, there is no question of adding further terms involving t_g^2 , t_g^3 , t_g^4 , . . . if more accurate experiments are performed. The fact is that the equation is an alternative definition of the constant volume hydrogen scale, and the equation serves as the basis for the calculation of the temperature at which the pressure is p . Now at the upper fixed point we have the following relation.

$$p_{st} = p_{ice} (1 + \alpha \cdot 100). \quad . \quad . \quad (5)$$

Re-writing equations (4) and (5) we have

$$\begin{aligned} p - p_{ice} &= p_{ice} \alpha t_g \\ p_{st} - p_{ice} &= p_{ice} \alpha 100 \end{aligned}$$

Dividing the one by the other, we have

$$\frac{p - p_{ice}}{p_{st} - p_{ice}} = \frac{t_g}{100}$$

which agrees with equation (3) defining the constant volume hydrogen scale.

It is important to compare and contrast the two scales in rather more detail. On the mercury-in-glass scale equal increments in temperature correspond to equal increases in length of the mercury column; on the constant volume hydrogen scale equal increments of temperature correspond to equal increments of pressure; on the mercury-in-glass scale 50°C. is *defined* to be that temperature at

which the mercury column is precisely half-way between its positions at 0°C and 100°C , the two fixed points, whereas on the constant volume hydrogen scale 50°C is *defined* to be such a temperature that the pressure of a given mass of hydrogen at constant volume is precisely half-way between its values at 0°C and 100°C . The question now arises, will these two scales of temperature agree at points other than 0°C and 100°C , where they agree by definition? It is simply a matter of whether the pressure of the hydrogen does happen to be exactly half-way between its values at 0°C and 100°C when the mercury column is just half-way between the 0°C and 100°C marks. This can only be settled by experiment, which shows that the two scales do not agree. The matter will be discussed later in this chapter, but even now we may ask why should they agree? After all, they are based on two quite unrelated properties of matter. From the practical point of view, we may say that the disagreement is less than 1°C for temperatures between 0°C and 100°C .

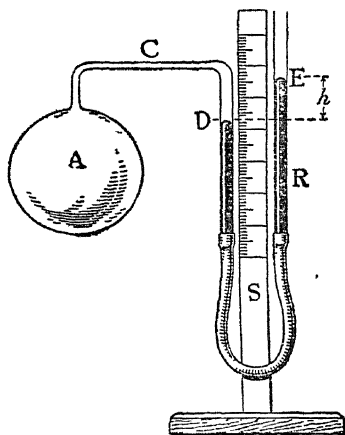


FIG 4

A simple type of constant volume thermometer due to Joly is shown in Fig 4. The bulb A contains a fixed mass of gas and is immersed in the body whose temperature is to be measured. It is connected by a capillary tube C to a mercury manometer. The volume of the gas is kept constant by maintaining the level of the mercury D at the same reading on the scale S by means of the movable tube R, and the pressure of the gas is given by

$$p = H + h,$$

where H = the height of the barometer

h = the difference in levels of D and E and is reckoned positive or negative according as E is above or below D.

Any unknown temperature is then determined as described above

5 Harker and Chappuis' Gas Thermometer.—Joly's thermometer has one serious defect, which can best be illustrated by a numerical example. Suppose $p_0 = 100$ cm, then for any gas $p_{100} = 136.6$ cm approximately. The increase in pressure for a rise in temperature of 100°C is 36.6 cm and so the change in pressure for a change in temperature of 1°C is 0.0036 cm. If we wish to measure temperature to 1°C , we must be able to measure the pressure of the gas to 0.004 cm. It is evident that Joly's thermometer cannot do this, however accurately the difference in levels may be read, since no barometer is incorporated with the instrument. The reading of the barometer may easily change by 0.01 cm in the time that elapses between observing it and the difference in levels of the thermometer, and if the barometer is at a different vertical height from the thermometer, a correction will have to be made to obtain the atmospheric pressure at the level of the thermometer from that read on the barometer. *So a really accurate constant volume thermometer always has a barometer incorporated in it*, and the instrument designed by Harker and Chappuis will now be described (Fig 5). It consists of a bulb A of about 1600 c.c. volume joined to the manometer by a capillary tube C. The gas is kept at constant volume by maintaining the level of the mercury in contact with the tip of the pointer P_1 , and so carefully is the apparatus designed that the volume of the dead space is only 0.5 c.c. (The "dead space" is the space occupied by that part of the gas which is not at the temperature to be measured, and so is roughly the capillary tube and the space over the mercury touching the pointer P_1). The pressure can be suitably adjusted by the reservoir R and is measured by a barometer B to which a scale is attached. The bulb is immersed in the body whose temperature is to be measured, and when the conditions are steady the reservoir is raised until the mercury just touches the tip of the pointer P_1 . The barometer tube is then adjusted by a screw mechanism until the level of the mercury in it just coincides with the tip of the pointer P_2 . Since the scale S is so arranged that its zero

coincides with the tip of the pointer P_2 , the reading of the vernier V , whose zero coincides with the tip of the pointer P_1 , gives the pressure of the gas directly. Two corrections must be applied (a) The gas in the "dead space" is not at the temperature to be measured. The error due to this is very small in this instrument and so an approximate determination of it is sufficient. (b) The volume of the gas is not constant owing to the expansion of the bulb. Here again the error is small and can be allowed for with sufficient accuracy.

The constant volume gas thermometer has several distinct advantages

(a) Wide range; it can be used from the liquefying point of the gas up to 1500°C .

(b) Accuracy; it will measure temperatures between the fixed points to 0.005°C , temperatures up to 500°C to 0.1°C , and temperatures as high as 1500°C to 2°C .

(c) Easily and accurately reproducible; this means that it is possible for two competent physicists, one working at Cambridge and the other at Melbourne, say, to make two constant volume hydrogen thermometers which will agree to the above limits of accuracy. This is due to the fact that the properties of pure hydrogen are the same all over the world, that pure hydrogen can be readily obtained, and that the properties

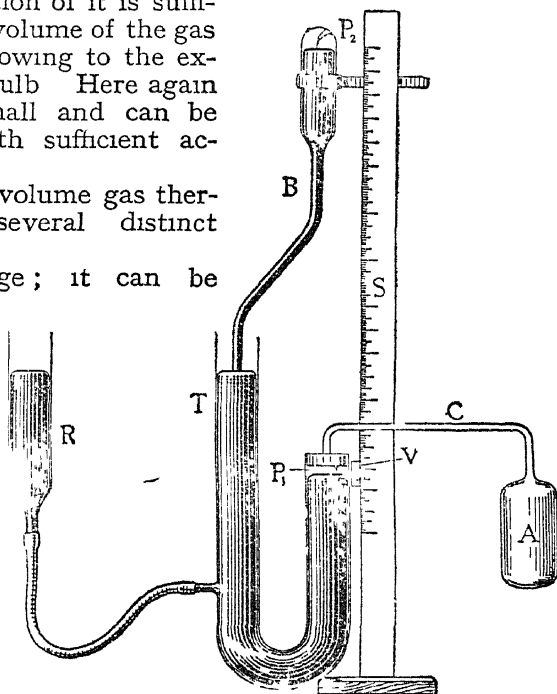


FIG 5

of the bulb, which do vary, only come in to a negligible extent. We have seen that different scales do not agree with one another, if this should turn out to be serious, then this last advantage of the gas thermometer will render it very suitable as the basis of a standard scale of temperature.

The gas thermometer has one very serious disadvantage; it can never be used for the direct measurement of temperature as its bulb is too large. Its great use is to serve as a standard for the calibration of more convenient types of thermometer, such as the *platinum resistance* and *thermo-electric thermometers*, which will now be described.

6. The Platinum Resistance Thermometer.—This thermometer depends on the fact that the resistance of a piece of platinum wire increases with temperature. It consists essentially of a suitably mounted coil of platinum wire, whose resistance can be measured at any temperature by a Wheatstone net arrangement. Let its resistance be R_{ice} , R_{st} , and R at 0°C , 100°C , and an unknown temperature respectively. Then we *define* the unknown temperature, t_p , on the platinum resistance scale of temperature by the equation

$$\frac{t_p}{100} = \frac{R - R_{ice}}{R_{st} - R_{ice}} \quad . \quad . \quad . \quad (5a)$$

Notice that yet another scale of temperature has been introduced, and that it is defined in just the same way as the others which have been considered, that is, equal increments of resistance *define* equal increments of temperature, or temperature is so *defined* that resistance varies uniformly with it. Furthermore, temperatures can be measured on the platinum resistance scale without the use of any other thermometer, for the determination of R_{ice} and R_{st} needs no thermometer. The question at once arises—do the platinum resistance and constant volume gas scales agree? Experiment shows that they do not and the discrepancy is serious. A numerical example will make this clear. Suppose $R_{ice} = 2.56$ ohms, then $R_{st} = 3.56$ ohms. If $R = 5.56$ ohms, then from equation (5a) $t_p = 300^{\circ}\text{C}$.; yet if the bulb of a constant volume hydrogen thermometer is placed in contact with

the same body it records a temperature of 309°C ! The situation may be summed up in this way, each new property of matter used for a thermometer introduces a new scale of temperature, which is shown by experiment to disagree with the other known scales. The only way to obtain concordant results with all of these thermometers is to choose one scale as a standard and calibrate all the other thermometers with reference to it. As we have not yet enquired as to the theoretical reason for the disagreement of different scales of temperature, our choice will be a purely *arbitrary* one dictated solely by *practical convenience and reproducibility*. The latter is the paramount consideration, whatever standard is chosen must be easily and accurately reproducible in any physical laboratory in any part of the world. Accordingly the International Bureau adopted as the *standard scale of temperature that given by the constant volume hydrogen thermometer, the gas to be at a pressure of 1 metre of mercury at 0°C* . The two fixed points are to be called 0°C and 100°C as usual. Notice that even the pressure of the gas at 0°C is specified, so that there is not a *single variable factor* which might cause two thermometers working on this scale to disagree.

We may now return to the platinum resistance thermometer. It has been shown experimentally by Callendar that the resistance R of a piece of pure platinum at a temperature $t^{\circ}\text{C}$ measured on the constant volume hydrogen scale is related to its resistance R_{ice} at 0°C by the equation

$$R_t = R_{ice} (1 + at + bt^2) \quad . \quad . \quad (5)$$

where a and b are constants. The thermometer is calibrated by finding R_{ice} , R_{st} and $R_{414.55}$. The latter is obtained by finding the resistance of the wire when it is at the temperature of the vapour from sulphur boiling at 1 standard atmosphere, 444.55°C being its temperature on the constant volume hydrogen scale as found by experiment. Substituting these values in equation (6) we have two relations from which a and b can be calculated, then any unknown temperature measured on the constant volume hydrogen scale can be determined from equation (6) once the corresponding resistance has been measured.

The thermometer bulb is a tube of porcelain T containing

a notched strip of mica *M* on which the coil of fine platinum wire is wound (Fig 6) The leads joining this coil to the Wheatstone net and the compensating leads *C* are insulated from one another by passing them through mica discs *D*, and the tube is exhausted of gas and sealed to avoid trouble due to oxidation The resistance *R* of the platinum coil is measured by the modified Wheatstone net arrangement shown in Fig 7 The resistances *P* and *Q* are made equal to one another, so that, when the bridge is balanced by means of the variable resistance *S*, $R = S$ It is necessary, however, to be able to measure the resistance *R* to 0.0001 ohm in order to determine a temperature to 0.01° C In the typical case considered above $R_{ice} = 2.56$ ohms, $R_{st} = 3.56$ ohms, and so a change in temperature of 0.01° C corresponds roughly to a change in resistance of

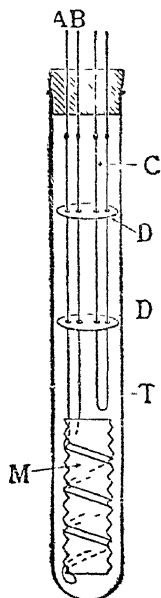


FIG 6

0.0001 ohm. Resistance boxes are not usually made with steps as small as this, so a uniform wire of length $2a$ and resistance r ohms per cm is inserted as shown The final balance is made by a sliding contact moving along this wire If it is in the position shown, then

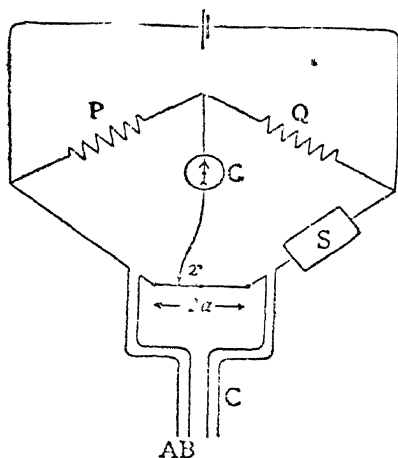


FIG 7.

$$R + (a - x)r = S + (a + x)r, \\ \therefore R = S + 2xr \quad . \quad . \quad . \quad (7)$$

But this relation takes no account of the resistance of the leads joining the platinum coil to the Wheatstone net, which will introduce an *error of the exposed column* which also occurred in the other two thermometers we have considered. In those it was corrected for, but in the platinum resistance thermometer Callendar devised a beautiful method of eliminating it. He inserted in the arm of the net opposite to the coil a pair of *compensating leads* exactly similar to those of the coil, he also laid these compensating leads by the side of the "real" leads so as to be at the same temperature. Since $P = Q$, it is obvious that the resistance of the compensating leads just cancels out that of the "real" leads and that equation (7) does give the resistance of the coil of platinum, the whole of which is at the temperature to be measured.

The advantages of the platinum resistance thermometer are

- (a) It is convenient to use in practice
- (b) It has a wide range, -200°C to 1200°C .
- (c) It is as accurate as the gas thermometer over the corresponding range

It has one disadvantage; it is not adapted to measuring varying temperatures, such as is required in obtaining the cooling curves of alloys. This is due to the large thermal capacity and low thermal conductivity of the bulb and to the time needed for balancing the bridge. The *thermo-electric thermometer* is admirably adapted to this purpose and will now be described.

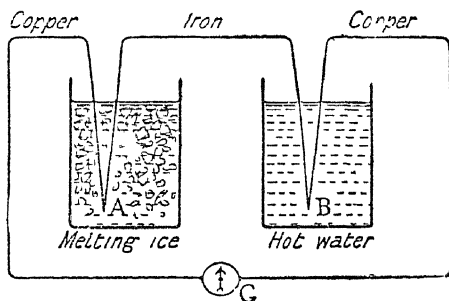


FIG 8

7. The Thermo-electric Thermometer.—Suppose any two metals or a metal and an alloy, such as copper and iron, are joined to form a circuit as shown in Fig 8, and one junction A is kept at the temperature of melting ice and the other B

is heated. It is found that the galvanometer G is deflected, showing that the difference of temperature of the junctions has given rise to an EMF which is causing a current to flow. It has been shown experimentally that this EMF is a function of the temperature difference between the junctions, and so this phenomenon, called the **Seebeck effect**, can be used to measure temperature. An arrangement for doing this is called a thermo-electric thermometer, two suitable substances are chosen, and the cold junction is kept in melting ice, while the hot junction is heated to various temperatures determined by a constant volume hydrogen thermometer, and the EMF at each temperature is measured. A graph of EMF against temperature of the hot junction on the constant volume hydrogen scale is drawn from these measurements, and the temperature of any body can be read off from it when the EMF of the thermo-electric thermometer has been measured with the hot junction in contact with the body.

For temperatures up to about $300^{\circ}C$ the most suitable substances for the thermometer are copper and constantan (an alloy of copper and nickel), because they give the comparatively large EMF of 40×10^{-6} volts per $^{\circ}C$ temperature difference between the junctions. Above $300^{\circ}C$ they become unreliable owing to oxidation and must be replaced by platinum and an alloy of platinum and rhodium which can be used up to $1600^{\circ}C$.

The method of measuring the EMF of the thermometer depends on the accuracy aimed at, a potentiometer is used if the temperature is to be measured with the greatest possible precision, but if only moderate accuracy is required a high resistance galvanometer will do. Its reading measures the current flowing, but this will be proportional to the EMF since the variation in resistance of the metals and leads is so small compared with the total resistance of the circuit. Where a measurement of temperature to the nearest $10^{\circ}C$ or so is all that is needed, thermo-electric thermometers are supplied with a high resistance galvanometer H calibrated directly in degrees Centigrade. The hot junction B is contained in a porcelain tube (Fig. 9) and is joined to the galvanometer by long, flexible leads;

no special arrangement is made to keep the temperature of the cold junction constant in this thermometer, which is used for measuring the temperature of blast furnaces and such like

The chief advantages of the thermo-electric thermometer are

(a) It can be used for measuring varying temperatures on account of its small thermal capacity

(b) It has a wide range, -200°C to 1600°C

(c) It can be made into a direct reading instrument.

But it is never quite so accurate as the platinum resistance thermometer at corresponding temperatures, for example, it will measure temperatures round and about 500°C to an accuracy of 0.3°C whereas the platinum resistance thermometer is accurate to 0.03°C

8. The Arbitrary Nature of Scales of Temperature—We are now in a position to consider what is meant by a scale of temperature in general terms, why different scales disagree, and hence why any scale is arbitrary

We have already seen (Art 1) that a scale of temperature based on a particular property of matter is defined by the equation

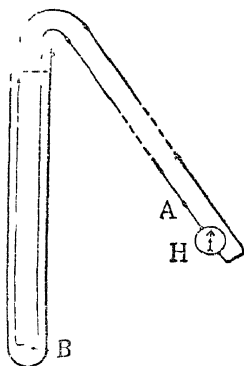


FIG 9

$$\frac{t_s}{100} = \frac{F - F_{ice}}{F_{st} - F_{ice}} \quad . \quad . \quad . \quad (1)$$

where F_{ice} , F_{st} , and F are the magnitudes of the given property at the lower and upper fixed points and the temperature, t_s , respectively. We shall call this the F scale of temperature. The fixed points chosen have been defined above, but it may be noted here that the proof of the fact that they are fixed needs no scale of temperature. It is only necessary to show that the value of the given property is always the same whenever the bulb of the thermometer is at the temperature of the fixed point and this can be done before any scale of temperature is thought of

It is evident from equation (1) that temperature is so defined that it varies uniformly with the selected property. This is so important that it will be shown in another way. If temperature is so chosen that it varies uniformly with the property chosen, then

$$F = F_{ice}(1 + a t_s) \quad . \quad . \quad . \quad (8)$$

where a is a constant independent of temperature

Then, at the upper fixed point, where $t_s = 100$, by definition,

$$F_{st} = F_{ice}(1 + a \cdot 100) \quad . \quad . \quad (9)$$

Equations (8) and (9) may be re-written

$$\begin{aligned} F - F_{ice} &= F_{ice} \cdot a \cdot t_s \\ F_{st} - F_{ice} &= F_{ice} \cdot a \cdot 100. \end{aligned}$$

Dividing one by the other

$$\frac{F - F_{ice}}{F_{st} - F_{ice}} = \frac{t_s}{100}$$

which agrees with our definition of temperature

Now choose another suitable property of matter, whose magnitude is F'_{ice} and F'_{st} at the lower and upper fixed points respectively. Then, on this scale, when its magnitude is F' the corresponding temperature t'_s is defined by the equation

$$\frac{t'_s}{100} = \frac{F' - F'_{ice}}{F'_{st} - F'_{ice}} \quad . \quad . \quad . \quad (10)$$

We shall call this the F' scale of temperature

Will the F and F' scales of temperature agree? That is, if the temperatures t_s and t'_s are those of the same body, will the numerical values of t_s and t'_s calculated from equations (1) and (10) be the same? This question can be answered by finding how F' depends on t_s and representing the results graphically. There are two alternatives, the relation between F' and t_s is either linear (Fig. 10) or non-linear (Fig. 11). In the first case A represents the value of F' at a temperature $t_s = 50^\circ \text{C}$; it is obvious that A lies half-way between the points representing F'_{ice} and F'_{st} ,

and that it will correspond to a temperature $t'_s = 50^\circ \text{C}$, the temperature scale t'_s being plotted on the graph on the assumption that temperature t'_s varies uniformly with F' . So in this case the scales agree at 50°C . and also at all

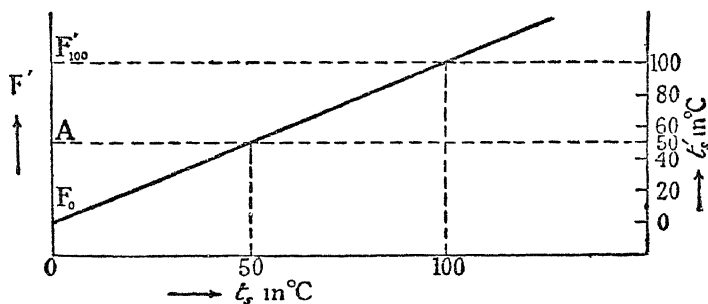


FIG 10

other temperatures as can easily be seen. In the second case B represents the value of F' at a temperature $t_s = 50^\circ \text{C}$; it certainly does not lie half-way between F'_{ice} and F'_{st} and so cannot represent a temperature $t'_s = 50^\circ \text{C}$, in fact it corresponds to a temperature $t'_s = 66^\circ \text{C}$ as the

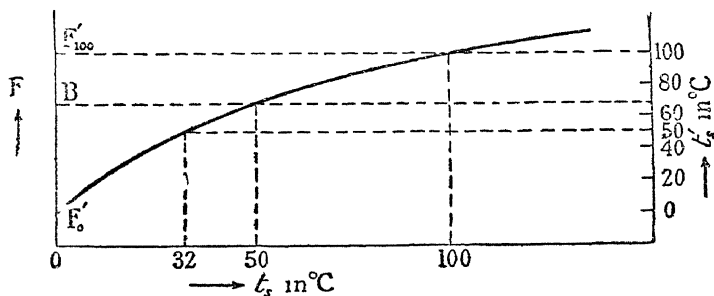


FIG 11

graph shows. Also it may be seen that a temperature $t'_s = 50^\circ \text{C}$ corresponds to $t_s = 32^\circ \text{C}$. Hence the two scales do not agree at this temperature, and a similar argument shows that they will disagree at every other temperature except the two fixed points, where they agree.

by definition. So we have the general principle that two scales of temperature will not agree unless the property on which the one is based varies uniformly with temperature measured according to the other. But there is no reason why this should ever be the case with properties of matter having little connection with one another and so different scales of temperature may be expected to disagree. And this is just the reason why the mercury-in-glass, constant volume hydrogen, and platinum resistance scales all disagree with one another. The disagreement for temperatures between the fixed points is not as marked as in the above example, which was purposely exaggerated, but it is due to the same fundamental reason and may be as big at temperatures of 1000°C . To consider a concrete example, the graph of Fig. 11 is very similar in shape to that showing the variation of the resistance of a piece of platinum wire with its temperature measured on the constant volume hydrogen scale and so as the resistance of platinum does not vary uniformly with temperature on this scale, the platinum resistance and constant volume hydrogen scales will not agree, as was pointed out when describing the platinum resistance thermometer. It was also mentioned in connection with the constant volume gas thermometer that the disagreement between the constant volume gas scale and the mercury-in-glass scale is small for temperatures between 0°C and 100°C , this is because the graph of the pressure of a gas at constant volume against temperature on the mercury-in-glass scale is almost a straight line between these two temperatures, in fact, the departure from linear form would not be detected by Joly's apparatus shown in Fig. 4.

This matter of the disagreement of different scales of temperature is so important that it will be illustrated by a numerical example. The opportunity may also be taken of pointing out that the difference in temperature of a body recorded by two thermometers working on different scales is an entirely different matter from the difference in reading between a Centigrade and Fahrenheit thermometer, the one is due to an inherent difference in the two properties on which the scales are based, whereas the other is merely due to a difference in the system of

graduation Let the following table give the resistance of a piece of metal wire at the corresponding temperature measured on the constant volume hydrogen scale

Resistance of Metal in ohms	5 00	5 15	5 28	5 40	5 51	5 61	5 70	5 79	5 87	5 94	6 00
Temperature in °C	0	10	20	30	40	50	60	70	80	90	100

Let us find the temperature on the metal resistance scale corresponding to 40° C on the constant volume hydrogen scale, and the temperature on the constant volume hydrogen scale corresponding to 70° C on the metal resistance scale

At 40° C on the constant volume hydrogen scale, $R = 5.51$ ohms Also $R_{100} = 5.00$ ohms and $R_0 = 6.00$ ohms Remembering that the resistance, R , of the metal is the property used in defining the metal resistance scale, we have from equation (1)

$$\frac{t_s}{100} = \frac{5.51 - 5.00}{6.00 - 5.00}$$

where t_s = temperature on the metal resistance scale corresponding to 40° C on the hydrogen scale

$$\therefore t_s = 51^\circ \text{C}$$

So a metal resistance thermometer would record the temperature of a body as 51° C when the hydrogen thermometer measured it as 40° C !

At 70° C on the metal resistance scale the resistance R of the metal is given by

$$\frac{70}{100} = \frac{R - 5.00}{6.00 - 5.00},$$

$$\therefore R = 5.70 \text{ ohms}$$

From the above table the corresponding temperature on the hydrogen scale is 60° C, so the metal resistance thermometer will read 70° C while the hydrogen thermometer indicates 60° C ! Discrepancies as marked as this are not found with most ordinary scales for temperatures within the fixed points, but they do occur at higher temperatures such as 500° C getting bigger the higher the temperature.

But the above example is not absurd, for the discrepancies would be greater than 10°C for temperatures within the fixed points in the case of a scale based on the vapour pressure of water and the hydrogen scale

We may sum up the position in this way scales of temperature based on the various properties of matter always disagree with one another to a greater or less extent. At present there is no justification for regarding any one property as more fundamental than the others and as all the scales disagree, they are all arbitrary. This difficulty is overcome from the practical point of view by selecting whichever scale may be most convenient as the standard scale of temperature and calibrating all thermometers with reference to it. We have seen above that the one chosen was the constant volume hydrogen scale, the gas to be at a pressure of 1 metre of mercury at 0°C . The practical reasons for this choice were given above, but there are also two others of great importance which can now be explained. Firstly, all gas scales, whether constant volume or constant pressure, show only very small disagreements with one another, of the order of 0.03°C , at temperatures between the fixed points and the disagreements decrease as the pressure decreases. There is reason to believe that all gas scales agree at infinitely low pressure, for the simple reason that all gases obey Boyle's law strictly under these conditions and so are all ideal gases. A scale of temperature based on the behaviour of gases at infinitely low pressure is certainly less arbitrary than, say, the mercury-in-glass scale, just because it depends on a property common to all gases and not on the property of one particular gas. So any gas scale is desirable as a standard because it is so nearly in agreement with this, the least arbitrary scale we have yet found. And secondly, the hydrogen scale is to be preferred to all others, because here the agreement is closest.

There is one problem that still awaits solution. It is intellectually unsatisfying to be compelled to use an arbitrary scale of temperature as our standard; we cannot be satisfied until we have found a scale of temperature *which is independent of the properties of any particular material substance*. Is the gas scale at infinitely low pres-

sure the one we are looking for? Is there anything in the nature of things to support its claim? An answer to these questions must be deferred for the present; but as we study each phenomenon in the subject, we must constantly search for the possibility of establishing a non-arbitrary scale of temperature, for we cannot rest content until we have reached this goal

EXAMPLES ON CHAPTER I

1 The mercury thermometer was the standard instrument for the measurement of temperature a hundred years ago, to-day it is almost obsolete. Discuss this statement

2 Give a full and critical account of Harker and Chappuis' constant volume gas thermometer

3 The pressure of the air in a constant volume gas thermometer is 80.0 cm and 109.3 cm at 0°C and 100°C respectively. The pressure is 83.0 cm at room temperature and 100.0 cm when the bulb is placed in some hot water. Calculate the temperature of the room and the hot water. On what scale are the temperatures measured?

Suppose you were given a simple constant volume gas thermometer, in which you could read the difference of levels to the nearest millimetre and could rely on the constancy of the barometer during readings to the same extent. To what accuracy could you measure a temperature with the instrument, if the pressure of the gas at 0°C is 70.0 cm?

4 Show how a scale of temperature is arrived at. Illustrate your answer by explaining exactly the meaning of the statement that mercury enclosed in glass expands uniformly with temperature (*Camb Schol*)

5 What is meant by a scale of temperature, and on what does the definition of any particular scale depend?

If alcohol is to be used as a thermometric liquid, how would you determine what temperature on the alcohol scale of temperature corresponds to 50°C ? (*O and C*)

6 Discuss the methods used for the measurement of temperature above the boiling-point of mercury (*O and C*)

7 Explain how temperature is defined on the scale of a constant volume air thermometer

The volume of a certain liquid at different temperatures is given by

$$V = V_0(1 + at + bt^2),$$

where $a = 0.01$, $b = 0.00003$, and t is the Centigrade temperature measured on the scale of a constant volume air thermometer. A thermometer is constructed with this liquid, its fixed points are determined, and the thermometer is calibrated as a Centigrade instrument. What temperature will this thermometer read when $t = 50^{\circ} \text{C}$? (*Camb Schol*)

8 Discuss the measurement of temperature, and explain how temperature is defined on the scale of a given type of thermometer.

When used to measure temperatures of about 300°C , the readings on the scale of an accurate mercury thermometer are about 2° higher than those of an accurate air thermometer. Why is this, and what reasons, if any, are there for adopting one scale rather than the other? (*O and C*)

9 Write a short account of methods of measuring temperatures (a) between 0°C and 100°C , (b) between 400°C and 600°C , and mention the chief errors in the methods you discuss. (*Oxford Schol*)

10 Describe as fully as you can a method of measuring high temperatures. (*Camb Schol*)

11 What is meant by a scale of temperature? Give a detailed account of the experiment you would perform to determine the temperature of boiling aniline on the platinum resistance scale of temperature. (*Camb Schol*)

12 Give an account of the construction and use of the platinum resistance thermometer, pointing out any special advantages of the instrument.

State, with reasons, the type of temperature-measuring device which you consider most suitable for use at temperatures of (a) -260°C , (b) -50°C , (c) 50°C , (d) 700°C , (e) 2000°C . (*London B Sc*)

13 Give the theory of a method by which temperatures on the constant volume hydrogen scale are calculated from the readings of a platinum resistance thermometer.

The resistance of such a thermometer is 2.56 ohms, 3.56 ohms, and 6.78 ohms at 0°C , 100°C , and 1445°C , the boiling-point of sulphur on the constant volume hydrogen scale, respectively. Calculate the temperature of boiling sulphur on the platinum resistance scale. When the bulb of the thermometer is placed in given liquid, the resistance is 5.23 ohms. Find the temperature of that liquid (a) on the platinum resistance scale, (b) on the constant volume hydrogen scale.

14 The melting-point of gold is 1062°C . Describe fully how you would verify this statement. (*Camb Schol*)

15 What is meant by a scale of temperature?

Give an account of the methods of measuring high temperatures (*Camb Schol*)

16 Describe the platinum thermometer and discuss its special merits. How is it calibrated? (*Tripes, Part 1*)

17 Describe a form of thermo-electric thermometer, and discuss its use as a means of measuring temperature

18 Discuss the parts played in the measurement of temperature by the gas thermometer on the one hand and the platinum thermometer and thermo-couple on the other

19 You are making a thermo-couple of copper and constantan, which has an E.M.F. of 4×10^{-5} volts per degree temperature difference between the junctions, when the cold junction is in melting ice. You wish it to measure temperatures up to 300°C to 0.1°C . You decide to use the potentiometer method and obtain a cell of E.M.F. 2 volts, a resistance box going up to 2000 ohms and a supply of uniform wire of resistance 0.0100 ohms per cm. You judge that you can fix the point of balance to the nearest 2 mm. What length of wire will you use for the potentiometer and what resistance will you put in series with it?

If you were given a galvanometer of 1000 ohms resistance, on which the smallest difference in current you can read is 10^{-7} amps, to what accuracy could you measure temperature with the above thermo-couple and this galvanometer?

20 Give an account of the various methods of measurement of temperature above 1000°C . (*Oxford Schol*)

21 Write a short essay on temperature. (*Oxford Schol*)

22 Explain clearly what is meant by a scale of temperature. Why do the mercury-in-glass and platinum resistance scales disagree, and hence why are the usual scales of temperature arbitrary?

The resistance of a metal wire at various temperatures on the mercury-in-glass scale is given in the following table

Temp in $^{\circ}\text{C}$	0	10	20	30	40	50	60	70	80	90	100
Resistance in ohms	5.00	5.01	5.05	5.21	5.30	5.40	5.52	5.62	5.74	5.87	6.00

Find the temperature on the metal resistance scale corresponding to 60°C on the mercury-in-glass scale, and the temperature on the latter corresponding to 30°C on the former

23 The following table gives the vapour pressure of water at various temperatures on the constant volume hydrogen scale

Vapour pressure in mm of mercury	4.6	17.5	55.1	149.2	355.1	760.0
Temp in °C	0	20	40	60	80	100

Find the temperature on the vapour pressure of water scale corresponding to (a) 20°C , (b) 70°C on the constant volume hydrogen scale. Find also the temperature on the constant volume hydrogen scale corresponding to (a) 67°C , (b) 464°C on the vapour pressure of water scale.

24. State clearly what is meant by a scale of temperature, and establish the conditions which decide whether two scales will agree or not. What steps have been taken to remedy the fact that the practical scales all disagree with one another?

CHAPTER II

SPECIFIC HEAT AND LATENT HEAT

9. Definitions.—Suppose some water A in a test-tube (Fig 12) is heated by a bunsen burner for 1 minute. Its temperature rises, and it is natural to enquire exactly how this happens. We can obtain some light on the process

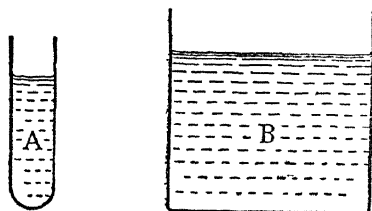


FIG 12

by considering a similar case. Suppose a bicycle tyre is flat, in order to pump it up to a suitable pressure it has to be supplied with air, which causes the necessary increase in pressure. It is obvious, in this case, that we cannot give the tyre pressure directly, for pressure is a

condition of the tyre. We have to give it a substance, air, which produces the required change in condition. The air and the resultant change in pressure are related to another as cause and effect. In the case of water being heated with a bunsen, we only observe the effect, but it is natural and

reasonable to suppose that in this case also *the change in condition* is due to a *substance* which the bunsen gives to the water. We call this substance **heat** and the only property at present attributed to it is that of causing a rise or fall in temperature when it is given to or taken from a body. There is no need to assume any other properties, such as that of being an invisible fluid, for they are not warranted by the evidence at present at our disposal. One body can give kinetic energy to another by collision, but this does not prove that kinetic energy is an invisible fluid. In the same way the fact that heat flows from one body to another does not prove that it is an invisible fluid. So we shall for the moment suspend judgment as to the further nature of this substance heat.

Now heat a larger mass of water B (Fig. 12) with the same bunsen as was used for A, burning at the same rate for the same time, 1 minute. It is found that the rise of temperature of A is much greater than that of B. This proves conclusively that the bunsen does not give temperature itself to A and B, otherwise the two rises of temperature would have been equal. For it is fair to assume that whatever the bunsen is giving to A and B it is giving in roughly equal amounts. So this experiment finally establishes the necessity for the existence of a thing called heat, distinct from and yet related to temperature. To sum up, heat and temperature are related to another as cause and effect, change in temperature is directly *observed*, whereas flow of heat is only *inferred*. Heat is a "thing" which causes a rise in temperature of any body to which it is communicated.

As soon as a new concept such as heat is firmly established, it is of the essence of the scientific spirit to seek to measure it in numbers. In this connection it is of interest to recall the words of Lord Kelvin: "When you can measure what you are speaking about and express it in numbers, you know something about it, and when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely in your thought advanced to the stage of a science." So we turn to methods of defining quantity of heat. Quantities of heat

are equal when they produce equal effects in equal masses of the same substance initially in the same state. A statement of this sort cannot be proved, nor can it be disproved. It is based on the belief in the *uniformity of nature*, that there is law and order in nature. This is the only article in the creed of the scientific man and it has now been abundantly justified by experience. So it requires equal quantities of heat to change equal masses of ice at 0°C to water at 0°C . This could be made the basis of the following definition of the unit quantity of heat: the unit quantity of heat is the amount of heat needed to change 1 gm. of ice at 0°C to water at 0°C . Again the quantities of heat needed to raise equal masses of a given substance from the same initial to the same final temperature are equal. This proposition led to a definition of the unit of heat, which is now universally accepted, the substance chosen being water and the standard mass being taken as the gram. So the unit quantity of heat is the amount of heat which raises 1 gm. of water through 1°C . It is called the **calorie**. It is true to say that the same quantity of heat is required to raise any 1 gm. of water from $t^{\circ}\text{C}$ to $(t + 1)^{\circ}\text{C}$, but it must be settled by experiment whether it is true that the same amount of heat is required to raise 1 gm. of water from 0°C to 1°C as from 50°C to 51°C or 72°C to 73°C . When this definition of the calorie is applied to calculate the amounts of heat given to A and B respectively in 1 minute by the bunsen, they are found to be equal within the limits of experimental error, thus proving that the same amount of heat is required to raise 1 gm. of water through 1°C at any temperature. So we shall adopt the above definition of the calorie for the present always bearing in mind that it may have to be modified in the light of more accurate experiments.

We now turn to the effect of heat on other substances. Is it true to say that equal quantities of heat produce the same rise in temperature in equal masses of all substances? Experiment shows that there is a different rise in temperature for every substance; in fact they all have a different capacity for heat from water and from each other.

The **thermal capacity** of a body is the amount of heat needed to raise its temperature through 1°C .

The **specific heat of a substance** is the amount of heat needed to raise the temperature of 1 grm of it through 1°C . The specific heat, then, is the thermal capacity of unit mass of the substance

Another term, the **water equivalent** of a body, is frequently used and may be defined as the mass of water whose thermal capacity is equal to that of the body itself. If a body has a mass m grm and is made of a substance of specific heat s , its thermal capacity is ms cal per $^{\circ}\text{C}$ and its water equivalent is ms grm

10. Determination of the Specific Heat of Solids and Liquids: The Method of Mixtures.—This is the

oldest and most fundamental method and is equally applicable to solids and liquids. The calculation of the specific heat is based on the principle that the sum of the heat lost by the hot bodies is equal to that gained by the cold. A cylinder R , of mass m and specific heat s is heated to a known temperature t_3 by immersing it in a steam bath. It is quickly transferred to a weighed calorimeter C containing a known mass of liquid, whose initial temperature,

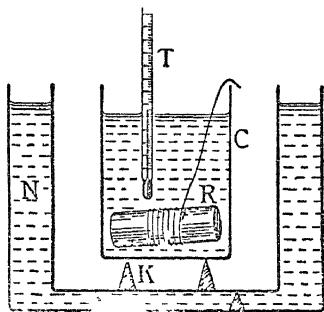


FIG 13

has just been measured by the thermometer T (Fig 13). The liquid is stirred well and the highest temperature reached, t_2 , is measured. The calorimeter stands on badly conducting knife-edges K to minimise loss of heat by conduction, and is surrounded by a constant temperature enclosure N so that conditions governing the loss of heat by "cooling" are steady. Then if s_1 is the known specific heat of the calorimeter, m_1 its mass, s_2 and m_2 the specific heat and mass respectively of the liquid, we have

$$ms(t_3 - t_2) = (m_1s_1 + m_2s_2)(t_2 - t_1). \quad \text{. (II)}$$

If the specific heat of the material of the cylinder R is required, then the liquid used is water, for which s_2 is 1, so s is the only unknown in equation (II) and can be

calculated at once. On the other hand, if the specific heat of the liquid is to be found, then a substance of known specific heat is used for the cylinder R and the equation now gives the value of s_2 .

There is one error common to all experiments involving the method of mixtures, which must now be dealt with. As soon as the temperature of the calorimeter rises above that of the surrounding water enclosure, it commences to lose heat in four ways

- (a) by conduction down the knife-edges;
- (b) by convection due to the surrounding gas;
- (c) by conduction through the surrounding gas;
- (d) by radiation

The effect of these losses, of which convection and conduction through the surrounding gas are perhaps the most serious, is to make the final temperature t_2 less than it would be on our assumption that all the heat from the hot bodies finds its way into the cold ones. It is necessary to calculate the temperature δt_2 , which must be added to t_2 to obtain the final temperature which would have been reached in the absence of the above losses. This quantity, δt_2 , is usually called the "radiation correction", this is an unfortunate and misleading name, as radiation in the strict sense of waves in the ether plays a negligible part in the process. So the quantity will be called the **cooling correction** in this book.

Various ways have been devised of finding or eliminating it. As some of them are only adapted to certain classes of experiment it will be most convenient to postpone an account of them until the appropriate experiment is described. Two of them are suitable for the type of experiment outlined above and will be dealt with now. The first method consists essentially in *eliminating* the error by keeping the temperature of the enclosure always equal to that of the calorimeter; this is most conveniently done by electrical heating.

In the second method the magnitude of the cooling correction is actually estimated and so equation (II) becomes

$$ms(t_3 - t_2) = (m_1s_1 + m_2s_2)(t_2 + \delta t_2 - t_1). \quad (I2)$$

The calculation of the cooling correction can only be done when the relation between the rate of loss of heat of a hot body and its excess temperature over that of the surroundings is known, and this problem will now be considered

11. Newton's Law of Cooling—Heat a copper calorimeter some two-thirds full of water to about 40°C , close the top with a lid to prevent evaporation and place it in a constant temperature enclosure as shown in Fig 13. Read the temperature of the water at suitable intervals of time and stir well. From these readings draw a graph of temperature against time, called a cooling curve, and determine the rate of loss of temperature at various temperatures by drawing tangents to the curve. Knowing the thermal capacity of the calorimeter and contents, the corresponding rate of loss of heat can be calculated and so a graph of rate of loss of heat and excess temperature of the calorimeter can be plotted. This is roughly a straight line, showing that the rate of loss of heat is proportional to the excess temperature. If the experiment is repeated, using different masses of water or different liquids to get different thermal capacities but always the same calorimeter so as to keep the area and nature of the cooling surface constant, then the same law is found to be true, and what is more important, the rate of loss of heat for a given excess temperature is the same in all cases. These results may be summarised by the following law "the rate of loss of heat of a hot body is proportional to its excess temperature over that of the surroundings, the constant of proportionality depending only on the nature and area of the cooling surface," or

$$-\frac{dH}{dt} = k\theta \quad . \quad . \quad . \quad (13)$$

where $-dH$ is the heat lost in a time dt when the excess temperature is θ , k being the constant of proportionality.

This is known as **Newton's law of cooling**, as it was discovered experimentally by him, one of the conditions laid down being that the hot body should be exposed to draughts. It is only true for excess temperatures up to about 30°C . and is entirely empirical. This is only to

to the heat lost by the calorimeter and contents in the interval of time DE. So it follows at once that the area A is proportional to the heat lost by the calorimeter and contents in the time QR, during which their loss of temperature is δt

$$c \delta t = kA \quad . \quad . \quad . \quad (14)$$

where c = the thermal capacity of the calorimeter and contents, k = the constant of proportionality in equation (13). Now applying precisely similar reasoning to the interval of time OQ, we have

$$c \delta t_2 = k A_2, \quad . \quad . \quad . \quad (15)$$

for the thermal capacity of the calorimeter and contents remains the same throughout the experiment, as does the area and nature of the cooling surface. Dividing equation (15) by equation (14) we have

$$\frac{\delta t_2}{\delta t} = \frac{A_2}{A} \quad . \quad . \quad . \quad (16)$$

from which δt_2 can be calculated. This quantity is the loss in temperature suffered by the calorimeter and contents by cooling in the time OQ, it is, in fact, the required cooling correction and its value is now substituted in equation (12), from which the unknown specific heat can now be calculated.

13. The Method of Cooling for Liquids.—Suppose a copper calorimeter nearly full of water standing in a constant temperature enclosure takes a certain time to cool from 70°C to 50°C , how long will the same calorimeter filled with about the same volume of glycerine take to cool between the same two temperatures? The specific heat of glycerine is about $\frac{1}{2}$, so the amount in the calorimeter has about half as much heat to lose as the water. At a given temperature it is losing it at the same rate, since the nature and area of the cooling surface and the excess temperature are the same in the two cases. Since the water and glycerine are cooled between the same two temperatures, the average rate of loss of heat will be the same for each, and therefore the glycerine will cool in about *half the time* taken by the water. It is the difference in

the specific heats of water and glycerine which is the ultimate cause of this difference in the times of cooling. Conversely, if the times of cooling are measured, they can be used to calculate the specific heat of glycerine knowing that of water. This is the fundamental principle of the determination of the specific heat of a liquid by **the method of cooling**. Two features of the method may be mentioned here; firstly, it is not applicable to solids, since they cannot be stirred to keep the temperature uniform and the cooling conditions constant. Secondly, the method does not depend on Newton's law of cooling, as will be shown below. Perhaps its chief use is to find an approxi-

mate value for the specific heat of a liquid at temperatures at which the method of mixtures is inconvenient, such as the specific heat of liquid naphthalene between 90°C and 110°C .

Weigh the copper calorimeter C empty (together with the stirrer S and the lid L), fill it nearly full of water, replace the lid and stirrer and weigh it again. Heat it up to about 80°C in a water-bath, so as not to

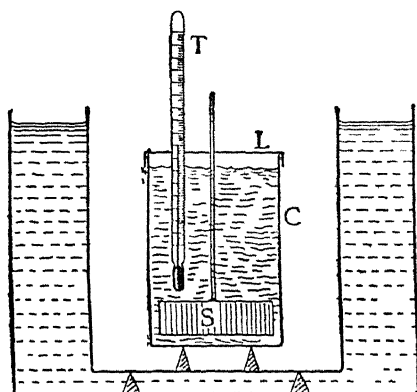


FIG 15

alter the nature of the cooling surface during the experiment, remove it and dry it, and then place it on badly conducting knife-edges in a constant temperature enclosure (Fig 15). Stir the water well the whole time by rotating the paddle-shaped stirrer, and take the time at which the temperature of the water is at suitable values, such as 70°C , 65°C , 60°C . The lid is used to prevent loss of heat by evaporation, which may even double the rate of loss of temperature in the case of water, and a rotary stirrer is used to avoid the loss of steam, which is inevitable with one which moves up and down. Now repeat the experiment, using an equal *volume* of the liquid of unknown specific heat, in order

that the area of the cooling surface may be the same in the two cases

We shall suppose that the water takes t_1 secs to cool from an excess temperature θ_1 to θ_2 , while the liquid occupies t_2 secs in cooling between the same two temperatures. If the water loses a quantity of heat dH in a time dt when the excess temperature is θ , we shall assume a general law of cooling such that

$$-\frac{dH}{dt} = k \cdot f(\theta)$$

where k is a constant depending only on the nature and area of the cooling surface; $f(\theta)$ is any function of the temperature, which means that there is a definite rate of loss of heat corresponding to each excess temperature and nothing more. The function need not be a simple algebraic or trigonometrical expression in θ , so that the law of cooling is a very general one. If Newton's law of cooling were true, for example, then $f(\theta) = \theta$. Now

$$-dH = -(ms + m_1) d\theta,$$

where m = the mass of the calorimeter,

s = its specific heat,

m_1 = the mass of the water,

$d\theta$ = the change in temperature in the time dt ,

the negative sign appearing because we are concerned with a loss of heat

$$\therefore \frac{(ms + m_1)d\theta}{dt} = -k \cdot f(\theta).$$

$$\therefore dt = -\frac{ms + m_1}{k} \frac{d\theta}{f(\theta)}.$$

$$\therefore t_1 = -\frac{ms + m_1}{k} \int_{\theta_1}^{\theta_2} \frac{d\theta}{f(\theta)}$$

Let

$$\int \frac{d\theta}{f(\theta)} = F(\theta)$$

$$\begin{aligned} \therefore t_1 &= -\frac{ms + m_1}{k} \left[F(\theta) \right]_{\theta_1}^{\theta_2} \\ &= \frac{ms + m_1}{k} \left[F(\theta_1) - F(\theta_2) \right]. \end{aligned} \quad (I7)$$

Now apply the same reasoning to the liquid of mass m_2 , specific heat s_2 . *Since the nature and area of the cooling surface is the same in its case, the constant k remains the same*

$$\begin{aligned}\therefore \frac{(ms + m_2s_2)d\theta}{dt} &= k f(\theta), \\ \therefore dt &= - \frac{ms + m_2s_2}{k} \frac{d\theta}{f(\theta)}, \\ \therefore t_2 &= - \frac{ms + m_2s_2}{k} \int_{\theta_1}^{\theta_2} \frac{d\theta}{f(\theta)},\end{aligned}$$

the limits of integration being the same as in the previous case since the liquid was timed between the same excess temperatures as the water.

$$t_2 = \frac{ms + m_2s_2}{k} [F(\theta_1) - F(\theta_2)] \quad . \quad (18)$$

Dividing equations (18) by equation (17) we have

$$\frac{ms + m_2s_2}{ms + m_1} = \frac{t_2}{t_1} \quad . \quad . \quad . \quad (19)$$

The interpretation of this equation is that the average rate of loss of heat is the same in the two cases, as has already been pointed out

All the quantities in equation (19) are known except s_2 , and so this can be calculated. The time taken by the water and liquid to cool over various temperature ranges can be obtained from the experimental observation, each temperature range furnishes data for a calculation of the specific heat of the liquid, so a number of such values can be determined from the results of the one experiment. We are able by this means to estimate the accuracy of the specific heat determined in this way. It may be noticed that no cooling correction enters into this method, since it is based on cooling. In conclusion, it may be emphasised that equation (19) is independent of Newton's Law of cooling and so the reliability of specific heats determined by this method is unaffected by the truth of that law.

14. Electrical Methods.—The most accurate method of determining specific heat is by the method of electrical

heating The fundamental principle is to heat the substance under test by passing an electric current through a suitably placed coil and measure the rise of temperature produced in a given time The heat supplied is given by

$$H = \frac{VCt}{J} \text{ calories}$$

where V is the P D in volts across the coil carrying a current C amperes for t secs, J being the number of joules in a calorie Knowing the mass of the substance, its specific heat can easily be calculated from these measurements The details of the method are different for solids, liquids, and gases, and so the three cases are treated separately in more convenient places later on (Arts 24, 85, 21)

15. The Measurement of Latent Heat. The Latent Heat of Fusion of Ice.—When a substance changes state, either from solid to liquid or liquid to gas, it is well known that three important effects occur

- (a) a change in volume,
- (b) no change in temperature,
- (c) a considerable absorption of heat

Thus heat does not manifest itself in the usual way by producing a rise in temperature, it is, as it were, *hidden*, its properties are suppressed as if it formed a chemical compound with the substance It is called **latent heat**, which means hidden heat, in contrast to "sensible heat," which can be felt by the rise in temperature which it produces It is now known that latent heat is necessary to supply the external work done by change in volume of the substance and the internal work required to separate the molecules against their mutual attractions

The latent heat of fusion of ice is the amount of heat required to change 1 grm of ice to water without change in temperature

The method of mixtures provides a simple and accurate way of finding the latent heat of fusion of ice A calorimeter of mass m and specific heat s containing m_1 grm of water is placed in a constant temperature enclosure as in Fig 13 The temperature t_1 of the water is noted and m_2 grm of dry ice at 0°C are added, the calorimeter

and contents are stirred until all the ice has melted, when the temperature t_2 is again measured. If L is the latent of fusion of ice, we have

$$m_2L + m_2t_2 = (ms + m_1)(t_1 - t_2)$$

from which L can be calculated

This experiment illustrates a third method of dealing with the cooling correction. The initial temperature of the water is adjusted to be as far above that of the enclosure as the final temperature is below it, so the calorimeter

and contents are losing heat to the enclosure in the first half of the experiment and receiving it in the second half. These amounts will be about equal, and so the cooling correction is eliminated.

The latent heat of fusion of ice is 80 calories per gram.

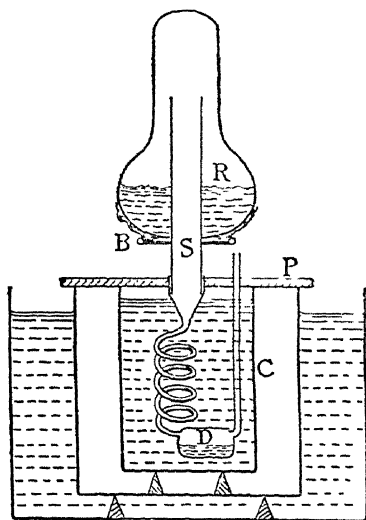


FIG 16

16. The Latent Heat of Vaporisation of Water.—

The latent heat of vaporisation of water is the amount of heat required to change 1 gram of water to steam without change in temperature.

The methods of finding this quantity can be divided into two classes

(a) those in which a known mass of steam raises the temperature of some water by being condensed in it,

(b) those in which a measured mass of steam is produced from water by electrical heating

As an example of the first class **Berthelot's method** will now be described (Fig 16). A calorimeter C containing water and fitted with a condenser D of known mass is placed in a constant temperature enclosure. Immediately after the temperature of the water has been

measured, the condenser is connected to the steam pipe S leading from the boiler R, and steam is passed into the condenser until the temperature of the cold water has risen to about 35°C . It must not be allowed to go above this, otherwise evaporation will commence. The steam supply is now cut off, the highest temperature to which the water rises is read by a thermometer (not shown in the diagram), and the condenser is removed and weighed to obtain the mass of steam condensed. The heat received by the calorimeter and contents from the burner B and the boiler is reduced to a minimum by a piece of wood P, covered with wire gauze, and the steam pipe is lagged with asbestos where it goes through the burner to prevent the steam from being superheated. The cooling correction is eliminated in this experiment by starting with the water as far below the temperature of the enclosure as it finishes above it. If m is the mass of the calorimeter and s its specific heat, m_1 and s_1 are the corresponding quantities for the condenser, m_2 is the mass of water in the calorimeter, M is the mass of steam condensed and t_1, t_2 , and t_3 are the initial and final temperatures of the calorimeter and contents and the temperature of the steam respectively, we have

$$ML + M(t_3 - t_2) = (ms + m_1s_1 + m_2)(t_2 - t_1)$$

from which L , the latent heat of vaporisation of water, can be calculated.

This method has two advantages over the ordinary condensation methods.

(a) The amount of condensation occurring before the steam actually reaches the cold water is reduced to a minimum by arranging for it to pass through boiling water almost until it reaches the calorimeter.

(b) The mass of steam condensed is more accurately determined with the use of a condenser than by measuring the increase in weight of the calorimeter and contents. For, if 10 grm of steam are condensed, this is measured as the difference between 30 grm and 40 grm if a condenser is used and the difference can be obtained with some accuracy. But it will be measured as the difference between 300 grm and 310 grm if the steam passes directly

into the water, and the small difference between two such large quantities cannot be as accurately determined as the same difference between 30 gram and 40 gram.

17. Henning's Electrical Method—We shall give only an outline of this method, the full details of which are outside the scope of this book. The water is contained in an air-tight bronze vessel B into which are sealed two tubes T and P (Fig 17). The former contains a thermo-

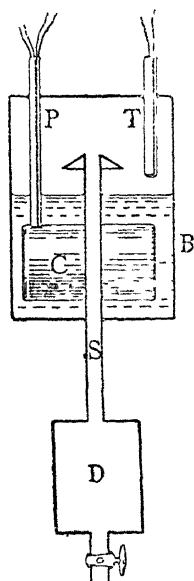


FIG 17

electric thermometer for measuring the temperature of the steam, and the latter carries the leads to the heating coil C, which is contained in an air-tight box and two other leads to the heating coil, which are used for measuring the P D between its ends. The water is boiled by passing a current through the heating coil and the steam passes down the pipe S, which has a conical shield at its upper end to prevent any drops of water from being splashed into it. The steam is condensed in the vessel D and issues as water from the lower end of it. When the rate of emission of the steam is steady, the water leaving the vessel D in a known time is collected and weighed, the current through the heating coil and the P D across it being noted at regular intervals. The cooling correction is eliminated by standing the vessel in an air space in an electrically heated oil-bath (not shown in the diagram) whose temperature is kept the same as that of the steam.

Let V = P D across the ends of the heating coil in volts,
 C = current in amperes flowing through it,
 M = Mass of water collected in t secs.

$$\therefore ML = \frac{VCt}{J}$$

from which the latent heat of vaporisation of water can be calculated. It is 536 calories per gram at 100°C , and

decreases with rise in temperature, presumably becoming zero at the critical temperature (Art 110) This method can easily be adapted to the determination of the latent heat of vaporisation of any volatile liquid

The high latent heat of many vapours is made use of in the process of refrigeration, two of the commonest refrigerants being ammonia and sulphur dioxide The liquid ammonia, say, is made to evaporate under reduced pressure drawing the latent heat required for this purpose from the brine-bath surrounding it The heat of the brine-bath is thus stored in the ammonia vapour, which proceeds to carry it away and give it up to the oil-bath surrounding the compressor, which liquefies it again The liquid ammonia is returned to the brine-bath and the cycle is repeated again and again, in this way the brine-bath can be kept at -30°C , while the oil-bath is so hot that the hand can hardly rest on it The brine-bath is used for manufacturing ice, which is then sold for the preservation of food and similar purposes Small refrigerators suitable for household use are very common in America and are coming into use in this country, the compressor being driven by an electric motor which works off the electric light mains The two main types of refrigerator are more fully described in Arts 59 and 134

18. The Determination of the Specific Heats of a Gas.
The Two Specific Heats of a Gas —When a gas is heated, there is, in general, both a rise in temperature and an increase in volume Each of these effects requires heat, in the former it goes to increase the heat energy or internal energy of the gas, whereas in the latter it supplies the external work done by the gas in pushing back the piston of the containing cylinder or the surrounding air It is evident, then, that the specific heat of a gas will depend on the conditions under which the rise in temperature takes place, that is, on how big the accompanying change in volume may be There will be, in fact, an *infinite number* of specific heats of a gas. Fortunately only *two* are important and they are the two simplest, namely, **the specific heat at constant volume** and **the specific heat at constant pressure**. The former, usually denoted by C_v , is the amount of heat required to raise 1 grm. of the gas through

1°C . while its volume is kept constant, and the latter, denoted by C_p , is the amount of heat required to raise 1 grm of the gas through 1°C while its pressure is kept constant. The specific heat at constant pressure is the greater, since, in this case, heat has to be supplied to do the external work consequent upon the expansion of the gas as well as to increase its internal energy.

19. The Specific Heat at Constant Volume : Joly's Differential Steam Calorimeter

The principle of this method is to find the mass of steam condensed in raising the temperature of a known mass of gas at constant volume to the temperature of the steam.

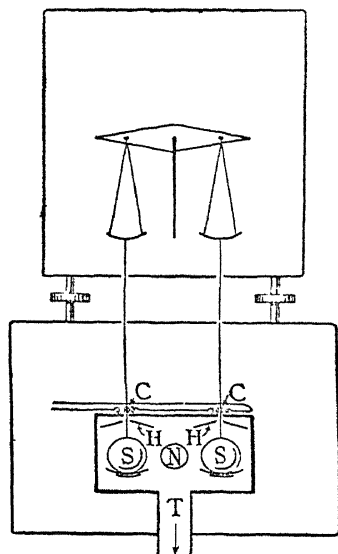


FIG 18

Two equal copper spheres S , about 7 cm in diameter, provided with pans to catch the drops of condensed steam, are suspended inside a steam chamber from the pans of a balance (Fig 18). Both spheres are exhausted and the balance is counterpoised, the left-hand sphere is then filled with the gas under investigation at the required pressure and the balance is counterpoised once more to find the mass of the gas. After allowing the gas to attain the temperature of its

surroundings, steam is admitted through the inlet pipe N to the steam chamber and condenses on both spheres until they are at the same temperature as the steam. A larger amount of steam condenses on the left-hand sphere than on the other because heat is required to raise the temperature of the gas in it, and the difference in the mass of steam condensed on the two spheres is equal to the mass required to heat up the gas alone, since the thermal capacities of the spheres are equal. This mass is found by adding

weights to restore the counterpoise of the balance, the counterpoise being tested two or three times at intervals of a few minutes while the chamber is full of steam to make sure that the condensation is complete. The initial temperature of the gas and the temperature of the steam are measured by sensitive standard mercury thermometers graduated over a small appropriate range

If m = mass of steam condensed to heat up the gas alone,

M = mass of gas,

t_1 and t_2 = initial and final temperatures respectively of the gas,

$$\therefore Lm = C_v M(t_2 - t_1)$$

It may be of interest to record that in a typical experiment with air at an initial pressure of 20 atmospheres, M was about 4 grm, and m was 0.12 grm for a rise in temperature of 85°C . Certain technical details of importance may be noticed here. Two shelters HH are placed over the spheres to prevent any drops of water condensed on the walls of the steam chamber itself from falling on to them. The holes by which the suspending wires leave the steam chamber are lined with plaster of Paris to prevent the formation of a drop of water, which would interfere with the swinging of the balance and make accurate weighing impossible. A further precaution consists in placing two electrically heated coils CC just over the holes to evaporate any drops of water which the plaster of Paris cannot absorb.

Two corrections have to be applied to the result obtained.

(a) The volume of the gas is not constant owing to the thermal expansion of the copper sphere, consequently the gas does work against the external pressure absorbing an equivalent amount of heat k . This can be calculated from a knowledge of the coefficient of expansion of copper and the initial and final pressures of the gas. The specific heat is then calculated from the equation

$$mL - k = C_v \cdot M(t_2 - t_1)$$

(b) It is impossible to obtain two spheres of equal thermal capacity. The error due to this is eliminated by repeating the experiment with the originally exhausted sphere now

filled with gas and taking the mean of the two results obtained as the corrected value of the specific heat

20. The Specific Heat at Constant Pressure: Regnault's Experiments.—Regnault performed a series of experiments in which he found the specific heat of a gas at constant pressure by the method of mixtures, the heat given out by the gas in cooling at constant pressure being measured by the rise in temperature produced in a known mass of water

The arrangement of his apparatus is shown in Fig 19. The gas under investigation was stored in the reservoir R, whose temperature was maintained at a known constant

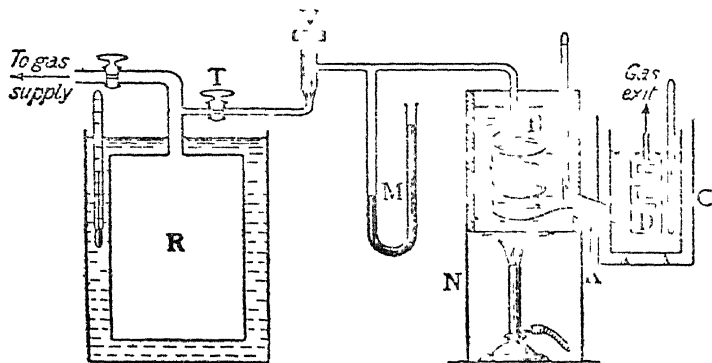


FIG 19

value by a water-bath. In performing an experiment, the tap T was opened and the screw valve V was adjusted to give a suitable difference in levels on the manometer M. This sets up a flow of gas through the apparatus, which must be maintained constant. This is done by opening the screw valve more and more, as the pressure of the gas in the reservoir goes down, so as to keep the difference in levels of the manometer M the same. The gas is heated up to the temperature of the oil-bath B by passing through a spiral coil immersed in it and its temperature is read from the thermometer standing in the oil-bath. It then goes on to the condenser D and heats up the water in the calorimeter C, finally entering the air after being cooled down.

to the temperature of the water. The difference in pressure of the gas before entering and after leaving the calorimeter, which was measured by two manometers (not shown in the diagram), was only 1 mm of mercury, and the error thus introduced is less than other experimental errors. The greatest possible care is taken to ensure that the gas is at the temperature of the oil-bath when it enters the calorimeter by continuing the bath almost to the calorimeter itself; at the same time the heat received by the calorimeter from the oil-bath is reduced to a minimum by surrounding each of them with wooden screens and by using badly conducting materials for the tube K joining them.

Let m_1 = mass of the calorimeter of specific heat s_1 .

m_2 = mass of the condenser of specific heat s_2

m_3 = mass of the water

m = mass of gas passing through the apparatus

t_3 = initial temperature of the gas

t_1, t_2 = initial and final temperatures respectively of the calorimeter and its contents

Since the flow of gas is constant, it cools on the average from t_3 to $\frac{t_1 + t_2}{2}$, and in doing so heats up the calorimeter and its contents from t_1 to t_2 .

$$\therefore C_p \quad m \left(t_3 - \frac{t_1 + t_2}{2} \right) = (m_1 s_1 + m_2 s_2 + m_3)(t_2 - t_1) \quad (20)$$

The mass of gas which has been used is found by measuring its initial and final pressures in the reservoir by a manometer (not shown in the diagram).

If the volume and temperature of the reservoir are v c.c. and t° C respectively, and the pressure of the gas falls from p_1 to p_2 cm. of mercury in the course of the experiment, we shall leave the reader to show that

$$m = \rho \frac{v}{273 + t} \frac{273}{76} (p_1 - p_2),$$

where ρ = the density of the gas at N.T.P.

Finally, this experiment illustrates the fourth method of making the cooling correction. In this case the calorimeter and its contents lose heat to the surrounding air

in the usual way, but they also receive heat by conduction down the pipe K leading out of the oil-bath and by convection, etc., from the screen N surrounding the oil-bath and its heater. The second factor is the greater and so the final temperature t_2 is too big. The quantity δt_2 to be subtracted from it to obtain the true value is determined in the following way. The rise in temperature of the calorimeter and its contents is measured for 10 minutes before the flow of gas is started, the oil-bath being kept at the same temperature as it will have while the gas is passing through it. The actual flow of gas is then commenced and continues for 10 minutes, when it is shut off and the rise in temperature of the calorimeter and its contents is measured during a further 10 minutes. During the first and last periods of 10 minutes, the calorimeter is receiving or losing heat from the various sources enumerated above, and the average of the two rises in temperature is equal to the required cooling correction δt_2 . Equation (20) now becomes

$$C_p \ m \left(t_3 - \frac{t_1 + t_2}{2} \right) = (m_1 s_1 + m_2 s_2 + m_3)(t_2 - \delta t_2 - t_1)$$

All the quantities in this equation have been measured or are known except C_p , which can now be calculated.

21. The Continuous Flow Method.—The principle of the continuous flow method of measuring C_p is to pass a steady stream of the gas under investigation over an electrically heated coil and measure the rise in temperature produced. Knowing the rate at which the heat is supplied and the rate of flow of the substance, its specific heat can be calculated. The method of **continuous flow calorimetry** was first devised by Callendar and Barnes, who applied it to finding the mechanical equivalent of heat and to the investigation of the variation of the specific heat of water with temperature. Callendar and Swann then applied it to the determination of the specific heat of a gas at constant pressure, and Scheel and Heuse subsequently performed some very accurate experiments by this method, an outline of which will now be given.

The whole apparatus, which is shown in Fig. 20, is surrounded by a water-bath, continuing some way along the

tube by which the gas enters. The electric current is turned on and the gas is set flowing at a constant rate through the apparatus. After passing by the platinum resistance thermometer A, it goes on through the double-walled jacket in the direction shown by the arrows and passes over the heating coil L, which raises its temperature. It then flows past a second platinum resistance thermometer B and leaves the apparatus. The tubes through which the gas flows are surrounded by a vacuum jacket, which makes the cooling correction negligible; if any heat should still escape from the gas in contact with the heating coil, it merely flows into the succeeding stream of gas which is coming down the inner wall of the jacket to the heating coil and so it is retained in the gas and does not ultimately get away. When a steady state is reached, the constant rise in temperature of the gas is found by taking the readings of the platinum

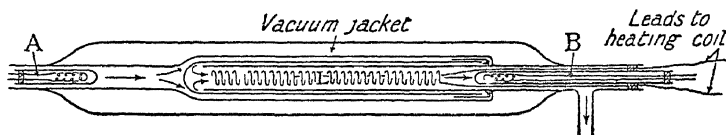


FIG 20

resistance thermometers. The heat supplied by the coil is determined by finding the P D between its ends and the current through it by methods which will be described in detail in connection with Callendar and Barnes' experiments on the mechanical equivalent of heat (Art 85)

Let V = the P D between the ends of the coil in volts

C = the current through it in amperes

m = the mass of gas flowing through the apparatus in unit time

$\delta \theta$ = the rise in temperature of the gas.

Then we have
$$\frac{VC}{J} = C_p m \delta \theta$$

from which C_p can be calculated.

The advantages of this method are :

(a) The temperature of all parts of the apparatus are constant when the readings are taken, so their thermal capacity is eliminated.

(b) As the temperatures are constant they can be read very accurately, say, to 0.001°C

(c) The rise in temperature can be made small, say, 4° or $^{\circ}\text{C}$, and so the method can be used to see if the specific heat varies with temperature

(d) The cooling correction is negligible except for the most accurate work, and even then it can be measured more accurately than in the other specific heat determinations, chiefly because it is more regular

The values of the two specific heats of various gases are given in Table I. It will be noticed that the specific heat at constant pressure is always substantially greater than that at constant volume. This is in accordance with our anticipations, and we shall see later that it is possible to give a quantitative explanation of the difference

TABLE I—THE SPECIFIC HEATS OF GASES

Gas	C_v Cals per gm per $^{\circ}\text{C}$	C_p Cals per gm per $^{\circ}\text{C}$
Hydrogen . . .	2.402	3.402
Air	0.172	0.242
Nitrogen . . .	0.175	0.235
Carbon dioxide	0.165	0.201

22. Results : Dulong and Petit's Law.—We have so far been concerned with an account of the methods of measuring specific heat. Having obtained the experimental facts, we must now seek to *classify* them, to see if we can express them, if possible, as a *mathematical equation*. At this stage only solids will be considered, no generalisation of any importance has been suggested in the case of liquids, and the treatment of gases is postponed until a theoretical explanation of their properties has been given (Ch. IX). **Dulong and Petit** first discovered a generalisation which applies only to elements in the solid state. They realised that no progress was likely to be made in the

attempt to classify the results of specific heats, until the thermal capacity of equal numbers of atoms was compared. So they turned to the **atomic heat** of the elements, which is the amount of heat required to raise 1 gram-atom of the element through 1°C and is given by the product of its specific heat and atomic weight. They enunciated the following law, which is named after them: "the atomic heat at constant volume of all elements in the solid state is about the same and equal to 6.0 calories per gram-atom per $^{\circ}\text{C}$ ". A list of the atomic heat at constant volume of the commoner elements at ordinary temperatures is given in Table II, and it can be seen that this law is a legitimate

TABLE II—THE ATOMIC HEAT OF ELEMENTS IN THE SOLID STATE MEASURED BETWEEN 15°C and 100°C

Element	Atomic Weight	Atomic Heat at Constant Volume, cals per gram-atom per $^{\circ}\text{C}$
Boron .	11.0	3.34
Carbon	12.0	1.36
Sodium	23.0	6.07
Aluminium	27.0	5.48
Silicon	28.3	5.07
Calcium	40.1	5.97
Iron	55.8	5.86
Copper	63.6	5.67
Zinc .	65.4	5.75
Silver	107.9	5.75
Cadmium	112.4	5.82
Iodine .	126.9	6.40
Mercury .	200.6	5.78
Thallium	204.4	6.33
Lead	207.2	5.91

generalisation or induction, to use the technical term, from the experimental facts. For the variation in atomic heat as we go through the list of elements in order of ascending atomic weight is not systematic; that is, it does not show a steady increase or a steady decrease. Also the range of variation in atomic heat which is the ratio of the largest

to the smallest value, is far less than that of the atomic weights.

We should say that it is the specific heat at constant pressure which is measured experimentally, but the specific heat at constant volume can be calculated from it. The specific heat at constant pressure of a solid is greater than that at constant volume because of the heat which must be supplied to pull the molecules of the solid further apart against their mutual attractions as it expands. We have tabulated the atomic heat *at constant volume* because that is the one which can be calculated theoretically, and because it is the quantity which is a true measure of the capacity of the body for heat.

But there are two serious objections to accepting this law as final. In the first place the atomic heats of boron, carbon, and silicon differ greatly from 6.0. This difficulty was explained away by the discovery that the atomic heats of these elements became much higher at about 500° C., and it was suggested that they would reach the value stated in Dulong and Petit's law at still higher temperatures. And this brings us to the second objection. The specific heats of all the elements vary to a greater or less extent with temperature; at what temperature, then, is the atomic heat to be measured for the purposes of Dulong and Petit's law? The position can be summed up by the statement that the law is a first approximation to the truth, it cannot, by its very nature, explain all the facts, for it takes no account of the variation of specific heat with temperature. But it is undoubtedly a step in the right direction, and it can be used as a starting-point for a more precise law. We may pause here to point out that this is a characteristic state of affairs in science, which finds its way to the truth by a series of successive approximations, each one more precise than the one preceding. A very good example of this is furnished by Newton's Inverse Square Law of Gravitation. This was regarded as final for some 200 years, but it has now been replaced by the Relativity Law of Gravitation due to Einstein, which is a closer approximation to the truth simply because it can explain all the facts which Newton's law explained and just those three or four outstanding at which the older law

failed But it is a mistake to say that the Newtonian Law of Gravitation is wrong; it is just as true as ever it was; the mistake lies in believing that it ever represented the final truth In Science we must keep an open mind and be willing to modify, or even reject, any theory in the light of new facts

After this digression we may return to Dulong and Petit's law Is it possible to explain it on any theory of the solid state? The theoretical explanation of this law is given in Chapter IX Starting with the assumption that heat is the energy of motion of the molecules of a body, the value of the atomic heat of the solid elements has been calculated and comes to 5.96 calories per gram-atom per °C So the experimental and theoretical values agree so well as to substantiate the application of the kinetic theory to this problem. There is, however, one serious disagreement; the theory predicts that the atomic heat should be independent of temperature, which is far from being the case And there the matter rested until Einstein put forward a new theory of specific heats which will now be considered

23. The Quantum Theory of Specific Heats.—The quantum theory was suggested in 1900 by Planck to account for fundamental laws of radiation which the classical theories of mechanics had completely failed to explain In 1906 Einstein applied Planck's ideas to the problem of the atomic heats of solid elements and his theory was later improved upon by Debye But they both make use of the same revolutionary idea, first suggested by Planck, that *energy is discontinuous* The implication of this statement may best be illustrated by an analogy A simple pendulum obeys the classical laws of mechanics and can have any amplitude, and so any energy, from zero upwards Suppose the pendulum were to obey Planck's law, then its energy could only have certain discrete values, and so only certain amplitudes differing from one another by a finite amount would be permitted As a matter of fact this is what the pendulum actually is doing; but since the energies permitted to a seconds pendulum only differ by 6.55×10^{-27} ergs, while its total energy may be 30,000 ergs for an amplitude of 1 cm, the permissible

amplitudes differ so little that all values appear possible. But when we come to consider the oscillation of an atom in a solid, whose total energy may be of the order of 10^{-8} ergs and whose permissible energies differ by 10^{-11} ergs, then the discontinuity of energy makes itself felt, and the possible amplitudes begin to differ by a comparatively discrete amount from one another. The discontinuity makes itself felt when the atom of energy, or quantum as it is called, becomes comparable with the total energy possessed by the system.

The classical theory of specific heats mentioned above assumed that the energy of an oscillating atom could vary continuously and could have any value. We have seen that it fails to give a complete explanation of the facts, and it occurred to Einstein that the quantum theory might succeed. He believed that the discontinuity in the energy and amplitude of the atomic oscillations, which cannot, of course, be detected directly, was the cause of the deviations from Dulong and Petit's law, and that the application of the quantum theory would lead to a complete explanation of the experimental facts. Both Einstein and Debye succeeded in obtaining a mathematical expression for the atomic heat of a solid element at constant volume and were able to make the following predictions:

(a) the atomic heat will increase with temperature and tend to the value 6 o, required by Dulong and Petit's law,

(b) the atomic heat will decrease as the temperature falls and tend to zero at the absolute zero,

(c) the nature of the variation of atomic heat with temperature will be the same for all elements, that is, *all the graphs of atomic heat and absolute temperature will coincide if the temperature scale is suitably adjusted*. That is

$$A = f\left(\frac{\theta}{T}\right) \quad . \quad . \quad . \quad (21)$$

where A = the atomic heat of an element (at constant volume) at the absolute temperature T ,

θ = a parameter, which is different for each element.

A parameter is a constant which can assume several values under different conditions. In this case θ is con-

stant for a given element, but varies from element to element $f\left(\frac{\theta}{T}\right)$ is zero at the absolute zero and tends to 60 at high temperatures. This theory gives a better explanation of the known facts than the classical theory; it explains why the atomic heats vary with temperature, and shows that the apparently abnormal cases of boron, carbon, and silicon are probably due to an unusually large value of the parameter θ . But it goes further than this; it makes definite predictions, and so it actually led to the work of Nernst and Lindemann on the specific heat of solids at low temperatures.

24. Nernst and Lindemann's Experiments.—Nernst and Lindemann used the method of electrical heating, the principle of which has been outlined in Art 14, although their experiments were designed for work at low temperatures, they can be used equally well at ordinary temperatures.

Two difficulties must be overcome in this type of experiment; firstly, the "cooling correction" (actually, of course, heat is *received* from the surroundings) becomes serious at low temperatures. It is eliminated by working with the calorimeter suspended in a vacuum. Secondly, as the variation of specific heat with temperature is being investigated, the rise in temperature of the calorimeter must be small; this suggests at once the use of electrical heating, in which the temperature changes are under complete control. The principal features of the apparatus are shown in Fig 21, and the details of the two types of calorimeter are illustrated in Figs 22 and 23. If the substance is a good thermal conductor, such as copper or silver, the calorimeter takes the form shown in Fig 22. A cylinder A of the substance is wound with a platinum coil E and screwed inside a hollow cylinder B of the same material. The coil is insulated from the inner cylinder by a thin sheet of paraffined paper and the narrow space of about 1 mm. between the two cylinders is filled with

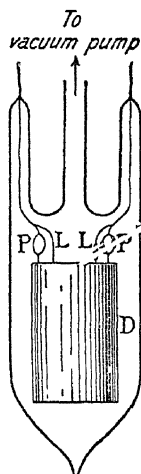


FIG 21

paraffin wax to supply further insulation. The calorimeter is suspended by the leads L to the coil, and these are insulated from the outer cylinder by the non-conducting loops P. If the substance is a bad conductor of heat, it is placed inside a hollow silver vessel V (Fig 23) on which the platinum coil E is wound. This is surrounded by a piece of silver foil F to prevent loss of heat from the coil to the surroundings and also to assist in distributing the heat evenly to the silver vessel. The narrow tube leading out of the vessel is sealed with a drop of solder before the calorimeter is suspended in the containing flask, in order to keep the air inside it; this air

is needed to help to distribute the heat from the walls of the silver vessel to the substance inside it.

The calorimeter is mounted in the containing flask, and brought to the required temperature by immersing the whole apparatus in liquid air, or liquid hydrogen for very low temperatures. The apparatus is then removed and

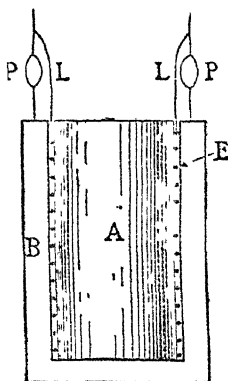


FIG 22

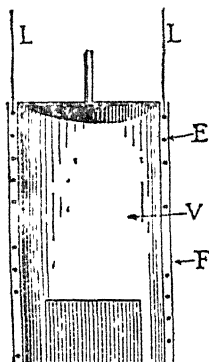


FIG 23

the flask is exhausted to a very low pressure, no change could be detected in the temperature of the calorimeter over a period of several hours, showing that the "cooling correction" had been completely eliminated. Heat is now supplied to the calorimeter by passing an electric current through the platinum coil, which also served as a resistance thermometer and measured the rise in temperature produced, which was usually about 1°C .

Let $V = PD$ across the coil in volts.

C = current in amperes flowing through it for a time t secs.

m = the mass of the calorimeter

δT = the rise in temperature produced

s = the specific heat of the substance at an absolute temperature T .

$$\frac{VCt}{J} = s \cdot m \cdot \delta T.$$

In the case of bad conductors an allowance must be made for the thermal capacity of the silver vessel and its coating of silver paper

The results of these experiments may be illustrated by a typical graph of atomic heat against absolute temperature

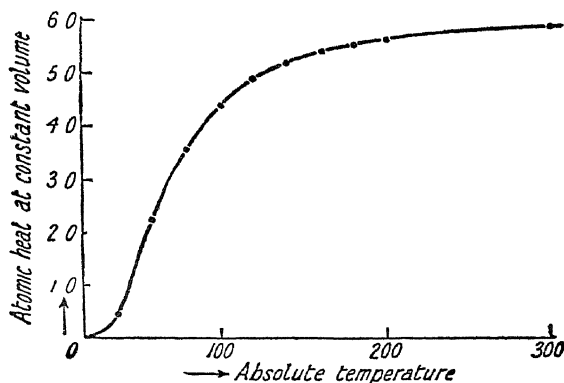


FIG 24

(Fig 24) They were a great triumph for the theories of Einstein and Debye, the three predictions mentioned above being accurately verified. The work described in this chapter forms an admirable example of the scientific method, in which—it cannot be too frequently emphasised—experiment and theory are always in close contact. First of all many experimental determinations of specific heats were made; then these facts were classified in the case of solid elements under Dulong and Petit's law, which was explained theoretically on the assumption that heat is the energy of molecular oscillation. The fact that the theory broke down in the case of boron, carbon, and silicon coupled

with the advent of the quantum theory led to its application by Einstein to this problem. His theory led to a search for new facts, as all theories should do, and these formed a striking verification of it. There is still some minor disagreement between theory and experiment, the final truth has not yet been reached. But there is no reason to anticipate that the removal of these disagreements will require any radical modification of the theory.

EXAMPLES ON CHAPTER II

1 Discuss the various methods of measuring the specific heats of solids and liquids, pointing out the advantages and disadvantages of the various methods (*Camb Schol*)

2 A copper calorimeter weighing 35.20 gm contains 105 gm of water at 16°C . Calculate the maximum temperature reached by the water if a cube of lead of 2 cm side, density 11.4 and specific heat 0.031, were heated to 150°C and dropped into the calorimeter.

How could you use the calorimeter and lead cube to determine the specific heat of benzene? Specific heat of copper = 0.092 (*Oxford Schol*)

3 A piece of iron of mass 20 gm was suspended in liquid air for some time, it was then quickly removed and suspended in water at 0°C . A coating of ice formed upon it and, when no further effect occurred, it was transferred with its coating of ice to a weighed beaker. The weight of the ice was found to be 3.93 gm. What was the temperature of the liquid air? Latent heat of fusion of ice = 80 cal/gm, specific heat of iron = 0.085 (*Oxford Schol*)

4 In 1 hour a petrol engine consumes 5 kilograms of petrol, whose calorific value is 10,000 cal/gm.

Assuming that 25 per cent of the total heat escapes with the exhaust gases and that 12 per cent of the heat is converted into mechanical energy, find the average horse-power developed by the engine and the initial rate of rise of temperature of the engine per minute. Radiation losses may be ignored, and the water equivalent of the whole engine is 40 kilograms (*Camb Schol*)

5 State Newton's law of cooling. Is it accurate at all temperatures?

A body initially at 80°C cools to 64°C in 5 minutes, and to 52°C in 10 minutes. What will be its temperature in 15 minutes, and what is the temperature of the surroundings? (*O. and C.*)

6 What considerations affect the rate of cooling of a body ?

Two bodies are of similar surfaces but are made of different materials, and they cool from 80°C to 40°C in 8 and 12 minutes respectively under the same conditions. If the weights of the bodies are 30 lb and 80 lb respectively, compare their specific heats (*Camb Schol*)

7 State Newton's law of cooling

If a body takes 3 minutes to cool from 100°C to 60°C , how long will it take to cool from 60°C to 20°C , assuming that the temperature of the surroundings is 10°C , and that Newton's law of cooling is obeyed ? (*Camb Schol*)

8 Discuss the "method of cooling" for the determination of specific heats, and show that the method is not dependent on the truth of Newton's law of cooling (*Camb Schol*)

9 Describe and explain how the specific heat of a liquid can be determined by observations on its rate of cooling

Two similar litre flasks are filled, one with mercury and the other with turpentine at the same temperature, and allowed to cool under the same circumstances. Which will cool the more rapidly, and for what reasons ? The specific heat of mercury is 0.033 and its specific gravity 13.5. The specific heat of turpentine is 0.41 and its specific gravity 0.87 (*O and C*)

10 What do you understand by the statement that the specific heat of aluminium is 0.2 cal per gm per $^{\circ}\text{C}$?

50 gm of water, contained in an aluminium vessel of mass 25 gm, is observed to cool at the rate of 1°C per minute when its temperature is 60°C . On repeating the experiment with an equal mass of oil, the rate of cooling at 60°C is found to be 2°C per minute. Find the value of the specific heat of the oil (*NUJB*)

11 A stream of water flows at a steady rate of 1 pint per minute through a copper pipe which is heated in the middle by a steady flame. The inlet and outlet temperatures are observed to be 10°C and 25°C respectively.

Another liquid of specific gravity 0.8 is now passed through the tube at a steady rate of $\frac{1}{2}$ pint per minute, and its initial and final temperatures are found to be 12°C and 61°C .

Calculate the specific heat of the liquid. What are the advantages and disadvantages of a calorimeter of this kind ? (*NUJB*)

12 Describe and discuss a method by which you could determine the latent heat of a metal which melts at about 200°C (*Oxford Schol*)

13 "Bismuth melts at 271°C ." Describe an experiment to verify this statement

When a quantity of liquid bismuth at its melting-point is transferred to a calorimeter containing oil the temperature of the oil rises from 12.5°C to 27.6°C . When the experiment is repeated with all the circumstances the same except that the hot bismuth is solid, the temperature of the oil rises to 18.1°C . The specific heat of bismuth is 0.032 cal per grm per $^{\circ}\text{C}$, what is its latent heat of fusion? (*NUJB*)

14 Describe an experiment to illustrate what is meant by latent heat

It was found by Black that a mass of 5 oz of ice-cold water suspended in a large hall rose to a temperature of 4°C in half an hour. An equal mass of ice in the same place took 10 hours to melt completely. Calculate from these data an approximate value for the latent heat of ice (*O and C*)

15 Give a critical account of Henning's electrical method of finding the latent heat of vaporisation of water, and say why you consider it superior to Berthelot's method

16 Define latent heat of evaporation of liquids and describe how it can be measured with accuracy. State Trouton's law connecting the latent heat of evaporation with the absolute temperature of the boiling-point (*Camb Schol*)

17 An electric current of 75 amp is passed for 30 minutes through a coil of wire of 12.4 ohms resistance immersed in benzene maintained at its boiling-point, 29.85 grm of benzene are found to have vaporised. Calculate the latent heat of vaporisation of benzene. Describe the apparatus you would set up in order to obtain observations of this kind (*Camb Schol*)

18 An exhausted copper sphere of mass 100 grm at 100°C is immersed in 150 grm of water at 10°C in a copper calorimeter of mass 150 grm. Find the final temperature, if the specific heat of copper is 0.1 cal per grm per $^{\circ}\text{C}$. The experiment is now repeated under the same conditions, except that the sphere is filled with 5 grm of air. Find the final temperature in this case, if the specific heat at constant volume of air is 0.172 cal per grm per $^{\circ}\text{C}$.

Use this example to show why it is difficult to obtain an accurate value for the specific heat of a gas at constant volume by the method of mixtures. Also show clearly how the difficulties involved have been overcome in Joly's method

19 Define specific heat, and explain why the specific heat of a gas at constant pressure is greater than that at constant volume. Give a critical account of Joly's method of finding the specific heat of a gas at constant volume

20 Discuss the principal errors in the measurements of specific heats by the ordinary calorimeter and the methods of eliminating or correcting them.

Describe the steam calorimeter (*Camb Schol*)

21 In a determination of the specific heat at constant pressure by Regnault's method, the gas is supplied from a reservoir whose volume is 30 litres at 10°C . The pressure of the gas is 6 atmospheres to start with and 2 atmospheres at the end, the temperature being 10°C throughout. The gas was heated to 150°C and led into a calorimeter at 10.0°C . The final temperature of the calorimeter and contents was 31.5°C and its water equivalent was 210 grm. If the density of hydrogen is 0.089 grm per litre at N.T.P., calculate its specific heat at constant pressure.

22 Compare and contrast Regnault's method and the continuous flow method for the determination of the specific heat of a gas at constant pressure.

23 What are the sources of error in calorimetric measurements and how are they allowed for? (*Oxford Schol*)

24 Discuss the various ways of dealing with the "cooling correction" in calorimetry, and state which you consider to be the most satisfactory.

25 Give a critical discussion of the way in which our knowledge of the atomic heat of elements in the solid state has developed since Dulong and Petit's law was enunciated.

26 What difficulties present themselves in an attempt to measure the specific heat of metals at low temperatures? Describe Nernst and Lindemann's work on this subject, pointing out how they overcame the difficulties you have mentioned.

27 Devise a method of measuring (a) the specific heat of liquid air, (b) its latent heat of vaporisation.

CHAPTER III

THE EXPANSION OF SOLIDS

25. Coefficient of Expansion.—Having established the fundamental conceptions of temperature and heat on a quantitative basis, it is natural to turn to an accurate investigation of the effects of heat. The commonest of these is expansion, and we shall describe the experiments on the expansion of solids in this chapter.

It is a matter of everyday observation that solids do expand when heated, and many examples may be quoted

of devices depending on or designed to overcome such expansion, such as the gaps in railway lines, the shrinking of steel tyres on to the wheels of railway engines, the compensated balance wheel of a watch in which one effect of heat is made to cancel the error due to another, and so on. The necessity for the solution of some of these practical problems stimulated interest in and research on the expansion of solids, and the results obtained, in some cases by disinterested workers with no thought of practical applications, have yielded a rich harvest in commerce in this as in many other fields of investigation. When a solid is heated between about 0°C and 100°C , it is found experimentally that the increase in length caused by a given rise in temperature is constant and independent of temperature, that is, its expansion is uniform. It is now necessary to define some quantity which is a measure of the expansion of a given material and quite independent of the size or shape of any particular specimen of it. The obvious choice is "the increase in length of unit length of the material when heated through unit rise in temperature" and is called the **coefficient of linear expansion of the substance**. Suppose a body of length l_0 cm at 0°C attains a length l_t cm when heated to $t^{\circ}\text{C}$, if its coefficient of linear expansion is α per $^{\circ}\text{C}$, then the increase in length is $l_0\alpha t$

$$\begin{aligned} \therefore l_t &= l_0 + l_0\alpha t \\ l_t &= l_0(1 + \alpha t) \quad . \quad . \quad . \quad (22) \end{aligned}$$

Temperature here is measured on the constant volume hydrogen scale, and the determination of the coefficient of expansion of solids is therefore something quite independent of and additional to that of temperature. This equation fits the facts for temperatures up to 100°C , but if the range is extended from -150°C to 500°C or more, then it is found that the expansion is no longer uniform, the increase in length for a given rise in temperature becoming greater the higher the temperature. The above equation must be replaced by one of the form

$$l_t = l_0(1 + at + bt^2 + ct^3 + \dots)$$

where $a, b, c \dots$ are constants of decreasing magnitude.

For the purpose of the rest of this discussion we shall assume that the range of temperature is so limited that equation (22) is applicable

There is one further point in connection with the theory of expansion which can be conveniently cleared up before the experimental work is described. Suppose a rod whose length is 100.00 cm at 0°C expands to 100.10 cm at 100°C ; then its coefficient of linear expansion is

$\frac{0.10}{100.00 \times 100} = 0.000010$ per $^{\circ}\text{C}$. Its length at 50°C is 100.05 cm. Suppose we are given this and the above coefficient of linear expansion and asked to find the length, l_{100} , at 100°C . Strictly speaking, it is untrue to say that

$$l_{100} = 100.05 (1 + 0.000010 \times 50) \quad (23)$$

because the coefficient of linear expansion we are using is the increase in length per $^{\circ}\text{C}$ rise in temperature of unit length at 0°C , whereas our length is measured at 50°C . We ought really to calculate the length at 0°C , l_0 , from the equation

$$100.05 = l_0 (1 + 0.000010 \times 50)$$

and use this value to calculate the length at 100°C . But let us see what error we shall make in using the "direct method". From equation (23)

$$l_{100} = 100.100025 \text{ cm}$$

But, by hypothesis, the true value is 100.10 cm. The error is quite negligible, that is, the difference in the two values is much smaller than could be detected by experiment, so we may use the "direct method" in calculating the length of a bar. This approximation is of such importance that it may usefully be considered in general terms. Let l_0 , l_1 , and l_2 cm be the lengths of a bar at 0°C , $t_1^{\circ}\text{C}$, and $t_2^{\circ}\text{C}$, respectively, then, if its coefficient of expansion is α per $^{\circ}\text{C}$, we have

$$\begin{aligned} l_1 &= l_0(1 + \alpha t_1) \\ l_2 &= l_0(1 + \alpha t_2) \\ \therefore \frac{l_2}{l_1} &= \frac{l_0(1 + \alpha t_2)}{l_0(1 + \alpha t_1)} \\ &= \frac{1 + \alpha t_2}{1 + \alpha t_1} \\ \therefore l_2 &= l_1 (1 + \alpha t_2) (1 + \alpha t_1)^{-1}. \end{aligned}$$

Expanding $(1 + \alpha t_1)^{-1}$ by the binomial theorem, we have

$$l_2 = l_1 (1 + \alpha t_2)(1 - \alpha t_1 + \alpha^2 t_1^2 - \dots),$$

$$\therefore l_2 = l_1 (1 + \alpha t_2 - \alpha t_1 - \dots)$$

But any terms involving α^2 or higher powers may be neglected, as their contribution to the value of l_2 is much less than experimental error

$$l_2 = l_1 \{1 + \alpha(t_2 - t_1)\} \quad . \quad . \quad (24)$$

which is the general equation corresponding to the particular case illustrated by equation (23). So we conclude that for all practical purposes the coefficient of linear expansion may be treated as independent of the initial temperature of the rod. We shall see later that, while the same thing is true for liquids, it is not so for gases solely on account of their much larger expansion.

26. Roy and Ramsden's Experiments.—In order to measure the coefficient of linear expansion of a solid, it is necessary to measure the increase in length of a known length due to a known rise in temperature. The numbers given in the above numerical example are typical for ordinary solids, and we see that the difficulty in this type of experiment is the measurement of the expansion. The problem resolves itself into the determination of changes in length of the order of 1 mm, the vernier and the micrometer at once suggest themselves. The latter is the more accurate, in the sense that an ordinary micrometer screw can be *read* to 0.002 mm, but this is useless unless it can be *set* to the same degree of accuracy. The ordinary methods, which involve an adjustment of the micrometer screw by the sense of touch, do not allow of such accurate setting. They can evidently be improved upon by employing the sense of sight to judge the coincidence of two fine lines—the most accurate adjustment of which the human body is capable and the only one which it should be called upon to make in accurate scientific work (Art. 1). In accurate experiments on the coefficient of linear expansion of solids the setting of the micrometer screw is done by observing the coincidence of the image of some cross-wires with those in the eyepiece of a microscope or

the coincidence of the image of a fine scratch on the bar with the vertical cross-wire of a microscope

Roy and Ramsden used the first method and their apparatus is shown in Fig 25. Three bars, P, Q, and R, are placed in troughs full of melting ice. Q is composed of the material under investigation and carries the objectives OO of two microscopes, P and R are standard bars of any suitable material and carry respectively vertical cross-wires CC, a known distance apart, and eyepieces EE, which are also fitted with cross-wires. The objectives can be moved along the length of the bar by means of two micrometer screws (not shown in the diagram) and at the beginning of the experiment they are so arranged that the images of the cross-wires CC as seen in their respective microscopes coincide with the cross-wires mounted in the eyepieces. The distance CC between the centres of the two cross-wires represents that length of the bar whose expansion is to be determined. The melting

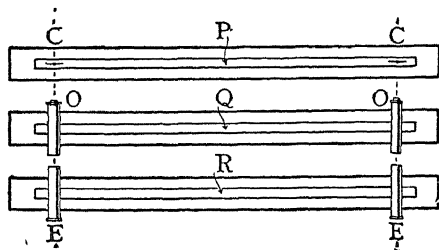


FIG 25

ice surrounding the bar Q is replaced by oil which is heated to a suitable temperature and causes the bar to expand and destroy the coincidence between the two pairs of cross-wires. The two objectives are now moved in through measured distances by the micrometer screws until the coincidences are restored and the sum of these distances is equal to the expansion of the bar. Knowing the temperature of the oil-bath, the coefficient of linear expansion of the bar can at once be calculated. This description differs in one or two details from Roy and Ramsden's actual experiments, but the underlying principle has been preserved. We may notice that the bars P and R, which serve to carry the "reference lines," as it were, against which the expansion is measured, are kept of constant length by being surrounded with melting ice during the whole experiment; some such

precaution as this must be observed in all experiments on linear expansion, for it is essential that the distance between the parts of the apparatus used to measure the change in length should not itself alter

27. The Comparator Method—This method is used at the International Bureau of Weights and Measures and exemplifies the second accurate way of setting the micrometer screw, namely, by observing the coincidence between the image of a fine line ruled on the bar and the cross-wire of a vertical microscope

The bar A under test and a standard bar are each mounted in a double-walled trough so as to be parallel to one another (Fig 26) The two troughs are mounted on a truck running on rails, so that the bars can be brought

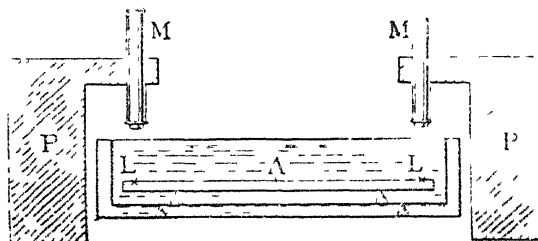


FIG 26.

in turn into the field of view of the microscopes MM, which are mounted in the massive stone pillars PP. The standard bar, whose temperature is kept constant

by surrounding it with water, which is in turn surrounded by a mixture of ice and water contained in the space between the walls of the trough, is brought underneath the microscopes MM. These are adjusted by micrometer screws (not shown) until the vertical cross-wire coincides with the corresponding line L ruled on the bar and the micrometers are read. The bar A is then wheeled into view and the microscopes are set on its lines and read. The mixture of ice and water in the outer compartment of the trough is now replaced by a circulation of water from a thermostat, thus raising the temperature of the bar to a suitable constant value. The microscopes are again set and read, and this process is continued until the expansion has been studied over a sufficient range of temperature. The increase in length of the bar for each

rise in temperature is given by the sum of the differences in the readings of the two micrometers, and so it can be seen if the bar expands uniformly, its coefficient of expansion can also be calculated. At the conclusion of the experiment the bar A is replaced by the standard bar and the microscopes are adjusted again. If the readings of the micrometers are the same as at the beginning, the distance between the microscopes has not been altered by heating up the bar A. If they are different, then this distance has altered and the appropriate correction must be applied. It is always very small as the microscopes are mounted in massive stone pillars, whose variations in temperature will be small on account of their large thermal capacity.

28. Fizeau's Method for Crystals.—The problem of measuring expansion becomes acute in the case of crystals, where it is important since crystals are just matter in a specially simple form and therefore in one specially suitable for theoretical investigation. We have seen that 100 cm. of the average metal expands about 1 mm. when heated through 100°C. , so a crystal 1 cm. long will expand about $\frac{1}{100}$ mm. when heated through the same range of temperature, if its coefficient of expansion is of the same order as that of metals. We cannot hope to get a specimen of a crystal more than 1 cm. long on the average, so we must devise a means of measuring an increase in length of $\frac{1}{100}$ mm. or even less in order to measure the coefficient of expansion of a crystal. A micrometer screw cannot measure such a length with any accuracy, so another method must be sought. It may be noticed that the length in question is about a hundred times greater than the wavelength of light, which suggests the trial of some method depending on this quantity. Fizeau was the first to devise such a method and his apparatus is shown in Fig. 27. Monochromatic light, from a cadmium or mercury-vapour lamp, issues from a point source S and is rendered parallel by a lens, after which it is reflected downwards by the glass plate G on to the air film bounded by the lower surface of the lens L and the upper surface of the crystal C. Interference occurs between the waves of light reflected from the lower surface of the lens and the upper

surface of the crystal, and if the microscope M is focussed on the air film, a series of concentric alternate dark and

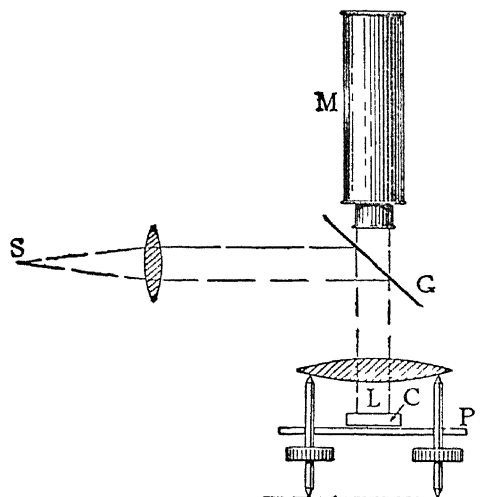


FIG 27

bright rings will be seen (Fig 28) They are called Newton's Rings, and their centre is at the point of least thickness of the air film. A description and explanation of this phenomenon is out of place in this book, but as a knowledge of it is essential to an understanding of this experiment, the reader is advised to consult any text-book on light if he is not already familiar with it. It is known that each ring is the locus

of points of equal thickness of the film, and also that the thicknesses corresponding to consecutive rings differ from one another by a distance equal to half the wave-length of light. If the lens is gradually raised the rings decrease in diameter, contract to a point, and ultimately disappear one by one. Finally the most important point for this experiment is that when the distance between the lens and plate has been increased by half a wave-length of light, one ring will succeed precisely the position of the next ring of smaller diameter. Therefore the change in distance between the lens and crystal due to a given rise in temperature can be calculated by counting the number of rings which pass a given point in the field of view of the microscope. As the wave-length of light is of the order of 6×10^{-5} cm and a motion of $\frac{1}{2}$ of a ring can easily be detected, expansions of the order of 6×10^{-6} cm. can be measured by this method.

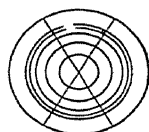


FIG 28

The procedure in an actual experiment is somewhat as follows. The thickness of the air film between the lens and crystal is adjusted to a suitable value by means of the levelling screws and Newton's rings are obtained. The temperature of the crystal and the polished table P on which it stands is read by means of a thermometer in contact with it. The crystal is heated by means of the furnace surrounding it (not shown) and the rings are counted as they move across the field of view. When the passage of a suitable number of rings has been observed, the heating is stopped and the temperature of the crystal is again measured. The difference in the expansion of the crystal and the part of the levelling screws projecting above the polished table P can now be calculated. The expansion of the levelling screws is known from the results of a similar experiment in which the crystal is removed and the rings are formed by the lens and polished table, so the expansion of the crystal itself can be obtained. From these data the coefficient of expansion of the crystal can be calculated.

29. Results and Applications.—The value of the coefficient of expansion of a number of common substances is given in Table IV at the end of this chapter, in order that the reader may appreciate the order of magnitude in various cases.

There is one important generalisation which can be induced from the results of the measurements of the expansion of isotropic metals, called **Grüneisen's law**, which states that the ratio of the coefficient of expansion and the specific heat of a metal is a constant independent of temperature. A few results are given in Table III, from Roberts' *Heat and Thermodynamics* to illustrate this law. It can be seen that both the specific heat and the coefficient of expansion decrease with decrease of temperature.

The many applications and illustrations of the expansion of solids may be divided into two classes, those in which expansion is a nuisance to be overcome and those in which it is used to produce some desired effect. It is of interest to deal with one or two of these applications here. Measurements of length are frequently made with a steel scale, as, for example, the height of the barometer, which is read at regular intervals at meteorological stations.

TABLE III—THE GRÜNEISEN LAW

Temperature in °C	$\alpha \times 10^6$	$\frac{\alpha \times 10^6}{C_p}$
ALUMINIUM		
- 173	13 6	107
- 100	18 2	109
0	23 0	110
100	24 9	112
300	29 0	119
438	29 8	112
COPPER		
- 87	14 1	174
0	16 1	177
100	16 9	180
400	19 3	179
600	20 9	182
SILVER		
- 167	15 0	319
- 87	17 1	329
0	18 3	327
100	19 2	331
500	23 1	350
800	26 0	342
PLATINUM		
- 150	7 4	269
- 100	7 9	268
0	8 9	280
100	9 2	277
875	11 2	267

Such scales are generally correct at 0° C, and so are incorrect at any other temperature. If the barometer is read at a temperature above 0° C, the height indicated by the scale will be too small, since the length between the centimetre marks is now greater than 1 cm. The ap-

propriate correction is easily calculated if the coefficient of expansion of the material of the scale is known

Precisely the same kind of error is encountered in the case of surveying, where the length of the base line is measured by a steel tape. This difficulty has now been overcome by a discovery due to M. Guillaume. He experimented for many years on the expansion of nickel-steel alloys and found that an alloy containing 36 per cent of nickel had a negligible coefficient of expansion, if it was subjected to only small changes of temperature. This alloy is called **invar** and is now used for making surveying tapes of constant length. M. Guillaume also discovered that an alloy with 45 per cent. of nickel had the same coefficient of expansion as glass and so could be used for "sealing-in wire" instead of platinum. This was a valuable discovery in view of the expense and increasing rarity of platinum.

We may now consider the effect of expansion on the rate of a pendulum clock. If it is adjusted to keep correct time in the winter, it will lose in the summer because the expansion of the pendulum rod will lower the centre of gravity of the pendulum and increase its periodic time. It is of interest to see how big the effect will be. We shall assume for the sake of simplicity that the clock is a simple pendulum, of which the wire is made of steel and which has a period of 2 sec. at 0°C . We shall proceed to calculate how much it will lose in a week at 20°C . The length of the pendulum at 0°C , l_0 , is given by

$$2 = 2\pi\sqrt{\frac{l_0}{g}}$$

If T = periodic time of the pendulum at 20°C ,

$$T = 2\pi\sqrt{\frac{l_0(1 + 0.000011 \times 20)}{g}},$$

0.000011 per $^{\circ}\text{C}$ being the coefficient of expansion of steel.

$$T = 2\pi\sqrt{\frac{l_0}{g}(\sqrt{1 + 0.000011 \times 20})},$$

$$\therefore T = 2 \sqrt{1 + 0.00022}$$

$$= 2 \times 1.00011$$

or

$$T = 2(1 + 0.00011) \text{ secs.}$$

Therefore in 1 00011 sec the clock is only moved on 1 sec. and so it loses 0 00011 sec

It is sufficiently accurate for our purpose to say that

in 1 sec the clock loses 0 00011 sec ,

\therefore in a week, the clock loses $0\ 00011 \times 3600 \times 24 \times 7$ secs
 $= 67$ secs

Consequently an ordinary pendulum clock which keeps correct time in the winter will lose about a minute a week in the summer due to the effect of expansion

This error due to expansion has been compensated out

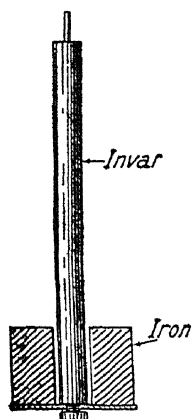


FIG 29

by means of expansion itself in a variety of ways, of which one is illustrated in Fig 29 In order that the clock shall keep correct time whatever the temperature, it is merely necessary to arrange for the constancy of the distance from the axis of rotation to the centre of oscillation, a point usually close to the centre of gravity The rod of the pendulum is made of a nickel-steel alloy and a hollow iron cylinder fits loosely over it and rests on a brass plate screwed to the bottom of the rod When the temperature rises the rod expands and lowers the centre of gravity of the pendulum, but the iron expands upwards and tends to raise the centre of gravity As the coefficient of expansion of iron is about twice that of the alloy,

these two effects can be made to cancel one another by suitably adjusting the length of the iron cylinder In actual practice the expansion is over compensated a little to eliminate one or two other minor errors which tend to make the clock lose in hot weather

It has been mentioned above that there are numerous cases in which expansion is a nuisance, as, for example, with railway lines These must be laid with gaps otherwise the enormous force of expansion would cause the line to buckle or break somewhere The magnitude of these forces may best be illustrated by an example Let us

consider the simple experiment to demonstrate expansion, in which a bar secured at one end by a screw and at the other by a short piece of cast iron is heated by a row of gas burners. The piece of cast iron is finally snapped in two; what force does the bar exert on it in doing this? The cast iron produces such a force as is required to change the expanded length of the bar into its original length. This can be found knowing Young's modulus for the bar. Suppose it is made of iron and is heated through 200°C to break the piece of cast iron. The increase in length per unit length due to this rise in temperature is

$$0.00011 \times 200 = 0.0022.$$

But we know that

$$\text{Young's modulus} = \frac{\text{stress}}{\text{strain}},$$

where stress = force per unit area,

strain = change in length per unit length.

Taking Young's modulus for iron as 13,500 tons per sq in. and the bar as 0.3 sq in in cross-section, we have

$$13,500 = \frac{\frac{F}{0.3}}{0.0022}$$

where F = the force which the cast iron must exert on the bar to prevent it from expanding

$$\begin{aligned}\therefore F &= 13,500 \times 0.0022 \times 0.3 \\ &= 8.9 \text{ tons}\end{aligned}$$

So when the bar breaks the cast iron it is exerting a force of about 9 tons on it!

30. Superficial and Volume Expansion—Suppose a rectangular metal sheet has a length l_0 and breadth b_0 at 0°C . If it is heated to $t^{\circ}\text{C}$ its length and breadth become l_t and b_t respectively, where

$$\begin{aligned}l_t &= l_0 (1 + \alpha t) \\ b_t &= b_0 (1 + \alpha t),\end{aligned}$$

α being the coefficient of linear expansion of the metal. Multiplying these two equations together, we have

$$\begin{aligned} l_t b_t &= l_0 b_0 (1 + \alpha t)^2, \\ A_t &= A_0 (1 + 2\alpha t + \alpha^2 t^2), \end{aligned}$$

where A_0 and A_t are the initial and final areas of the sheet respectively

But $\alpha^2 t^2$ may be neglected as its contribution is less than the experimental error in experiments on expansion,

$$A_t = A_0 (1 + 2\alpha t)$$

But, as with linear expansion, we may write

$$A_t = A_0 (1 + \beta t),$$

where β = coefficient of superficial, or area, expansion of the metal

Comparing these two equations, we see that

$$\beta = 2\alpha,$$

that is, within the limits of experimental error, the coefficient of superficial expansion of a metal is twice its coefficient of linear expansion

A similar relation may be derived in the case of volume expansion. Suppose we have a rectangular metal block whose sides are of length l_0, b_0, d_0 at 0° C. and l_t, b_t, d_t at t° C. Then

$$\begin{aligned} l_t &= l_0 (1 + \alpha t), \\ b_t &= b_0 (1 + \alpha t), \\ d_t &= d_0 (1 + \alpha t), \end{aligned}$$

$$\begin{aligned} \therefore l_t b_t d_t &= l_0 b_0 d_0 (1 + \alpha t)^3, \\ \therefore V_t &= V_0 (1 + 3\alpha t + 3\alpha^2 t^2 + \alpha^3 t^3), \end{aligned}$$

where V_0 and V_t are the initial and final volume of the block respectively

But $3\alpha^2 t^2$ and $\alpha^3 t^3$ may be neglected for the same reason as before,

$$\therefore V_t = V_0 (1 + 3\alpha t).$$

But we may write

$$V_t = V_0 (1 + \gamma \cdot t),$$

where γ = coefficient of cubical expansion of the metal.
Comparing these two equations, we have

$$\gamma = 3\alpha,$$

that is, within the limits of experimental error, the coefficient of cubical expansion of a metal is three times its coefficient of linear expansion

TABLE IV — COEFFICIENT OF LINEAR EXPANSION OF SOLIDS
BETWEEN 0° C AND 100° C

Substance	Coefficient of Linear Expansion per °C $\times 10^6$
Aluminium .	24 0
Copper .	16 5
Cast iron .	10 2
Steel . .	11 0
Lead . .	27.6
Platinum .	9 0
Silver . .	18 8
Brass . .	18 9
Invar . .	0.9
Soft glass .	8 5
Diamond .	1 2
Quartz axis	7 5
⊥ axis	13 7

EXAMPLES ON CHAPTER III

N B — The numerical values of coefficients of expansion should be obtained from Table IV

1 Enumerate the weak points in a simple laboratory method you have performed of finding the coefficient of linear expansion of a solid, and show how they are remedied in one of the standard methods

2 Discuss the Comparator method for finding the coefficient of linear expansion of a solid Compare and contrast it with Roy and Ramsden's method

3 An iron chain 22 yd long is supplied for marking out a cricket pitch If its length is correct at 50° F, what error will a groundsman make if he uses it at 90° F. ?

4 A barometer is supplied with a steel scale correct at 0°C . The height of the barometer reads 75.342 cm when the temperature of the scale is 10.5°C . What is the correct height of the barometer?

Suppose a rod, whose true length at 15.0°C is 25.00 cm, is measured with this steel scale at 15.0°C . What will the length of the rod appear to be on this scale?

5 Railway lines are laid with gaps to allow for expansion. If the gap between steel lines 66 ft long is 0.50 in. at 10°C , at what temperature will the lines just touch?

6 The expansion of a given material can be represented by the equation

$$l = l_0 (1 + at + bt^2),$$

where $a = 15 \times 10^{-6}$ per $^{\circ}\text{C}$ and $b = 4.0 \times 10^{-8}$ per $^{\circ}\text{C}$. If measurements are being made to 1 in a 1000, find *above* what temperature it is no longer permissible to omit the term bt^2 in calculating the length l from l_0 , the length at 0°C ?

7 A seconds pendulum is one which completes half an oscillation in 1 second. Such a pendulum is made of invar and is correct at 10°C . If the average temperature for the three months of June, July, and August is 25°C and the clock is correct at 12.0 a.m. on June 1st, by how much will it be incorrect at 12.0 a.m. on September 1st?

8 Discuss the measurement of the coefficient of expansion of crystals, and state briefly the character of the results obtained.

9 A steel plate is 80.0 cm long and 50.0 cm wide at 10°C . Calculate its area at 100°C (a) from first principles, (b) assuming that the coefficient of superficial expansion of a metal is twice its coefficient of linear expansion. Hence find the percentage error involved in the assumption made in the second case.

10 If a crystal has a coefficient of expansion of 13×10^{-7} in one direction and 231×10^{-7} in every direction at right angles to the first, calculate its coefficient of cubical expansion (Lond. B.Sc.)

CHAPTER IV

THE EXPANSION OF LIQUIDS

31. The Relation between Temperature and Density.

—Since a liquid has no shape, we are concerned only with its **coefficient of cubical or volume expansion**, which is

defined as the increase in volume of unit volume of the liquid due to unit rise in temperature. If, as is usually the case, the liquid expands uniformly, the coefficient of expansion decreases with rise in temperature of the initial volume of the liquid. But, as in the case of solids, this decrease may be neglected in all except the most accurate work, where it is usual to measure the initial volume at 0°C and to work with the corresponding coefficient of expansion. If a volume V_0 of liquid, whose coefficient of expansion is α , suffers a rise in temperature t , its volume becomes V_t , where

$$V_t = V_0 (1 + \alpha t) \quad . \quad . \quad . \quad (25)$$

In treating of the expansion of liquids it is more convenient to deal with *density* than volume, the former being the more fundamental quantity. Suppose m is the mass of the volume of liquid considered above, then its initial and final densities, ρ_0 and ρ_t respectively, are given,

$$\rho_0 = \frac{m}{V_0}, \quad \rho_t = \frac{m}{V_t}$$

Substituting the values of V_0 and V_t derived from these equations in equation (25) above, we have

$$\begin{aligned} \frac{m}{\rho_t} &= \frac{m}{\rho_0} (1 + \alpha t), \\ \therefore \rho_t &= \rho_0 (1 + \alpha t) \quad . \quad . \quad . \quad (26) \end{aligned}$$

This is the fundamental equation relating the density and temperature of a liquid and will be the starting-point of all the formulæ derived in this chapter.

32. The Expansion of a Hollow Vessel.—Before we can proceed to describe the various methods of measuring the coefficient of expansion of a liquid, we must find how the volume of a hollow vessel will change with temperature. This can be done theoretically in the following way. Suppose that the vessel is rectangular in shape, the internal length of its sides being l_0, b_0, d_0 . If it is heated through $t^{\circ}\text{C}$, they will become l_t, b_t, d_t respectively, where

$$\begin{aligned} l_t &= l_0 (1 + \lambda t), \\ b_t &= b_0 (1 + \lambda t), \\ d_t &= d_0 (1 + \lambda t). \end{aligned}$$

λ being the coefficient of linear expansion of the walls of the vessel. Multiplying these three equations, we have

$$l_t b_t d_t = l_0 b_0 d_0 (1 + \lambda t)^3$$

We may neglect terms in $\lambda^2 t^2$ and $\lambda^3 t^3$ as being less than the experimental error

$$\begin{aligned} \therefore l_t b_t d_t &= l_0 b_0 d_0 (1 + 3\lambda t), \\ \therefore V_t &= V_0 (1 + 3\lambda t), \end{aligned}$$

where V_0 and V_t are the initial and final volumes of the vessel respectively

But $3\lambda = g$, where g = the coefficient of cubical expansion of the walls of the vessel

$$\therefore V_t = V_0 (1 + gt)$$

Therefore the vessel expands in the same way and to the same extent as a solid body of the same size, shape, and material.

This has been proved above for a vessel of simple shape, and it can be shown in a similar way that it is true for a vessel of any shape

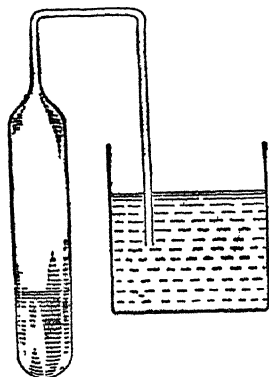


FIG 30

33. The Weight Thermometer.—It can be seen from equation (26) that it is only necessary to compare the density of a liquid at two different temperatures in order to measure its coefficient of expansion. The specific gravity bottle at once suggests itself as a simple way of doing this, and the weight thermometer is merely a specific gravity bottle specially adapted to this type of experiment. It consists of a glass bulb with one end drawn off

as shown in Fig 30. It is dried, weighed empty, and filled with liquid in the following way. The bulb is warmed over a bunsen to drive out some of the air and the nozzle is dipped in a beaker of the liquid, some of which is drawn in by cooling the bulb. The liquid is then boiled so that its vapour may drive out all the remaining air, and the

thermometer fills completely when the bulb is cooled sufficiently to cause the vapour to condense. It is important to use liquid which has been boiled to remove any traces of dissolved air, and even then an air bubble may appear when the thermometer has been filled. This must be expelled by boiling away some of the liquid and filling the thermometer again. It is now cooled to the required initial temperature by immersing the bulb in a cold-water bath, the nozzle being kept in the liquid the whole time. The nozzle is removed from the liquid and any drop adhering to it is taken off by a filter paper, after which the thermometer is removed from the water-bath, dried, and weighed. It is then heated to the desired temperature in a water-bath, the liquid being removed from the nozzle by a filter paper as it oozes out. When the liquid has ceased expanding, the thermometer is taken out of the water-bath, dried, and weighed again.

The theory of the method is as follows.

Let M = the mass of the weight thermometer empty.

M_0 = its mass when full of liquid at the initial temperature

M_t = its mass when full of liquid at the final temperature

t = the rise in temperature

V_0 and V_t = the volume of the weight thermometer at the initial and final temperature respectively

ρ_0 and ρ_t = the density of the liquid at the initial and final temperature respectively

α = the coefficient of absolute expansion of the liquid

g = the coefficient of cubical expansion of the material of the weight thermometer.

Now

$$\rho_0 = \frac{M_0 - M}{V_0},$$

$$\rho_t = \frac{M_t - M}{V_t} = \frac{M_t - M}{V_0(1 + gt)},$$

$$\therefore \frac{\rho_0}{\rho_t} = \frac{M_0 - M}{M_t - M}(1 + gt).$$

But, from equation (26),

$$\begin{aligned}\frac{\rho_0}{\rho_t} &= 1 + \alpha t, \\ \therefore 1 + \alpha t &= \frac{M_0 - M}{M_t - M} (1 + g t), \\ \therefore \alpha &= \frac{M_0 - M_t}{M_t - M} \frac{1}{t} + \frac{M_0 - M}{M_t - M} g\end{aligned}$$

If we ignore the expansion of the containing vessel, that is, if we put $g = 0$, then α becomes α_p , the coefficient of apparent expansion of the liquid, or its coefficient of expansion relative to the containing vessel. It follows from the above equation that

$$\alpha_p = \frac{M_0 - M_t}{M_t - M} \frac{1}{t}, \quad . \quad . \quad . \quad (27)$$

$$\therefore \alpha = \alpha_p + \frac{M_0 - M}{M_t - M} g \quad . \quad . \quad . \quad (28)$$

A simple example will show that for many liquids it is permissible to put $\frac{M_0 - M}{M_t - M} = 1$, even if the weight thermometer is made of glass, for which $g = 0.000025$ per $^{\circ}\text{C}$. In the case of glycerine $\alpha_p = 0.000480$ per $^{\circ}\text{C}$ and $\frac{M_0 - M}{M_t - M} = 1.04$ will be typical values. Using the accurate formula,

$$\begin{aligned}\alpha &= 0.000480 + 1.04 \times 0.000025 \\ &= 0.000480 + 0.000026 \\ &= 0.000506 \text{ per } ^{\circ}\text{C}\end{aligned}$$

If we put $\frac{M_0 - M}{M_t - M} = 1$,

$$\begin{aligned}\alpha &= 0.000480 + 0.000025 \\ &= 0.000505 \text{ per } ^{\circ}\text{C}\end{aligned}$$

The difference in these two values is less than the experimental error of the routine laboratory experiment, so for such experiments we may re-write equation (28) in the form

$$\alpha = \alpha_p + g \quad . \quad . \quad . \quad (28a)$$

Therefore it is *approximately* true to say that the coefficient of absolute expansion of a liquid is equal to the sum of its coefficient of apparent expansion and the coefficient of cubical expansion of the containing vessel. But it is necessary to emphasise that this is only an approximation, the validity of which must be examined in each individual case.

The measurements we have made so far enable us to calculate α_a , the coefficient of apparent expansion of the liquid, from equation (27). We can see from equation (28) that we require to know g , the coefficient of cubical expansion of the material of the weight thermometer, in order to calculate α , the coefficient of absolute expansion of the liquid. The various ways of finding g will be discussed later on in this chapter.

34. Matthiessen's Method.—As the density of a liquid can be measured by **Archimedes' principle**, it is possible to devise a method of finding the coefficient of expansion of a liquid by the same means. This was carried out by Matthiessen in his investigation of the expansion of water and can be applied equally to any other liquid.

A sinker, which may be a glass rod or sphere, or a bulb of some suitable material weighted with lead shot, is weighed in air and then immersed in the liquid and weighed again. The liquid is heated through a suitable rise of temperature and the sinker is weighed once more. It is best to suspend the sinker outside the balance case by a thin wire passing through a hole in the bottom to prevent the inaccuracy in weighing which would result if the beaker of hot liquid were inside the balance case.

Let M = the weight of the sinker in air

M_0 = its weight immersed in the cold liquid.

M_t = its weight immersed in the hot liquid

t = the difference in temperature of the hot and cold liquid

V_0 and V_t = the volume of the sinker when cold and hot respectively. The rest of the notation being the same as in Art. 33, we have

$$\rho_0 = \frac{M - M_0}{V_0},$$

$$\rho_t = \frac{M - M_t}{V_t} = \frac{M - M_t}{V_0(1 + gt)},$$

$$\therefore \frac{\rho_0}{\rho_t} = \frac{M - M_0}{M - M_t} (1 + gt).$$

But, from equation (26),

$$\frac{\rho_0}{\rho_t} = 1 + \alpha t,$$

$$\therefore 1 + \alpha t = \frac{M - M_0}{M - M_t} (1 + gt),$$

$$\therefore \alpha = \frac{M_t - M_0}{M - M_t} \frac{1}{t} + \frac{M - M_0}{M - M_t} g. \quad \cdot \quad (29)$$

As in Art. 33

$$\alpha_p = \frac{M_t - M_0}{M - M_t} \frac{1}{t},$$

where α_p = the coefficient of apparent expansion of the liquid,

$$\therefore \alpha = \alpha_p + \frac{M - M_0}{M - M_t} g$$

Again, it is *approximately* true to write

$$\alpha = \alpha_p + g$$

All the quantities in the expression for the coefficient of apparent expansion have been measured in the experiment and so it can be calculated, but we cannot find the coefficient of absolute expansion of the liquid unless the cubical expansion of the sinker is known. It will be remembered that we encountered the same difficulty in the case of the weight thermometer, and we shall now describe various ways of finding the expansion of the containing vessel or sinker.

35. The Determination of the Coefficient of Absolute Expansion.—The methods of finding this quantity fall into two classes, those which involve a knowledge of the expansion of the containing vessel and those which do not. In the first class the coefficient of apparent expansion of the liquid is found by one of the two methods described above. The coefficient of cubical expansion of the weight thermometer or sinker is found in a separate experiment by measuring the linear expansion of a specimen of the material

of which it is made, and using the relation that the cubical expansion is three times the linear. This method assumes that the coefficient of expansion of a material such as glass is unaffected by the heat treatment which is involved in making a bulb out of a piece of tubing. Experiment has shown that this is not true, so the method has had to be abandoned in the case of glass, but it can still be used with fused silica on account of its small coefficient of expansion, 0.0000015 per °C. A typical value for the coefficient of apparent expansion of mercury relative to fused silica is 0.0001804 per °C. From equation (28a)

$$\begin{aligned}\alpha &= 0.0001804 + 0.0000015 \\ &= 0.0001819 \text{ per } ^\circ\text{C}\end{aligned}$$

Now the coefficient of cubical expansion of fused silica as determined above will be accurate to at least 10 per cent, and an error of this magnitude will cause an inaccuracy of less than 1 in 1000 in the value of the coefficient of expansion of mercury, which is adequate for all but the most accurate work.

A second method determines the coefficient of expansion of the containing vessel after it has actually been made. It consists in measuring the coefficient of *apparent* expansion relative to the containing vessel of a liquid, such as mercury, whose coefficient of *absolute* expansion has already been found by one of the methods which are independent of the expansion of the containing vessel. The cubical expansion of the vessel can then be calculated from equation (28a).

36. Dulong and Petit's Method for the Absolute Expansion of a Liquid.—We have seen in the previous article that it is important to devise a way of finding the coefficient of absolute expansion of a liquid which is independent of the expansion of the containing vessel. This means that a method of comparing densities must be utilised which is unaffected by any change in size of the containing vessel. The method of equilibrating columns at once suggests itself (Fig 31). If some mercury is placed in the U-tube, whose limbs need not be of the same diameter, it will come to rest at the same level D and F in the two limbs. Now pour h_1 cm of a liquid of density ρ_1 into

one limb and add a height h_2 cm of a liquid of density ρ_2

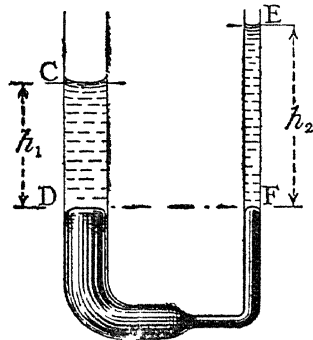


FIG 31

to the other so that the two mercury surfaces are again at the same level. It is found that these two heights of liquid will balance one another whatever the diameter of the limbs of the U-tube. The pressure at C = the pressure at E (atmospheric) and the pressure at D = the pressure at F, because they are the same horizontal level in a liquid at rest. Therefore the pressure of h_1 cm of one liquid is equal to that of h_2 cm of the other. Remembering that pressure is force per unit area, we have

$$h_1 \rho_1 = h_2 \rho_2, \quad \frac{\rho_1}{\rho_2} = \frac{h_2}{h_1}$$

By measuring the heights h_1 and h_2 , we can compare the densities of the two liquids without requiring to know anything about the area of cross-section of the limbs of the U-tube.

Dulong and Petit balanced a column of hot liquid against a column of cold, and since the ratio of these heights is independent of the diameter of the limbs of the U-tube, it is independent of the expansion of the one containing the hot liquid. If H_0 and H_t are the heights of the cold and hot columns respectively,

$$H_0 \rho_0 = H_t \rho_t,$$

where ρ_0 and ρ_t are the densities of the cold and hot liquid respectively.

$$\therefore \frac{\rho_0}{\rho_t} = \frac{H_t}{H_0}$$

From equation (26)

$$\frac{\rho_0}{\rho_t} = 1 + \alpha t, \quad \therefore \frac{H_t}{H_0} = 1 + \alpha t, \quad \therefore \alpha = \frac{H_t - H_0}{H_0 \cdot t}. \quad (30)$$

Dulong and Petit performed their experiments with mercury and their apparatus is illustrated in Fig 32. It consists of a U-tube containing mercury, whose upper ends are wide in order to reduce the depression of the mercury due to surface tension to a minimum. One limb is enclosed in an oil-bath whose temperature is measured by a constant volume gas thermometer with a long bulb to get the mean temperature of the bath, while the other is surrounded with melting ice. The cross-piece is arranged to be accurately horizontal, and when

the temperatures are steady a little mercury at 0°C is added to the cold column, if necessary, until the level in the hot column just projects above the oil-bath. The difference in levels of the hot and cold columns is measured by a cathetometer and the height of the cold column is also found. We must decide from what point to measure this height. It is

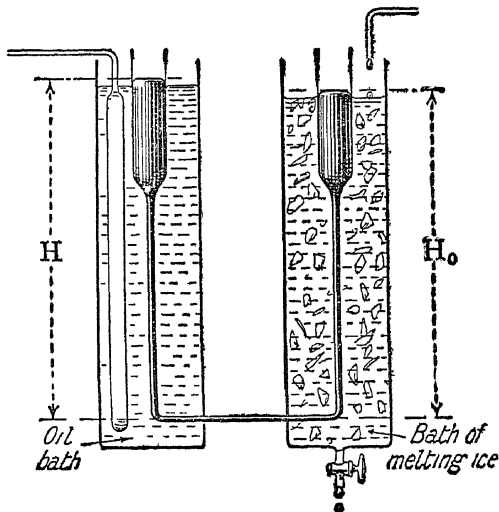


FIG 32

clearly from the level in the cross-piece at which the pressure in the two limbs is the same. A little thought will show that this is at B, the level which coincides with the axis of the cross-piece (Fig 33). It follows that the pressure in the hot column is greater than that in the cold at the level C and less at A. Consequently there is not equilibrium over the whole of the cross-piece, but only at the level B; there is, in fact, a feeble convection current flowing in the direction indicated by the arrows the whole time. The cross-piece is made as narrow as possible in order to keep this convection

small and to reduce the error due to the uncertainty of the position of B to a minimum. All the quantities on the right-hand side of equation (30) having been measured, α can at once be calculated. It may be emphasised in conclusion that that equation contains no term involving the expansion of the containing vessel, and so the method gives directly the coefficient of absolute expansion of mercury.

37. Regnault's Method.—It can be seen that Dulong and Petit's method, while simple, is subject to the following errors —

(a) A small portion of each mercury column has to project above its constant temperature bath in order that its height may be read.

(b) The two mercury surfaces are at different temperatures, and so their respective depressions due to surface tension will be different.

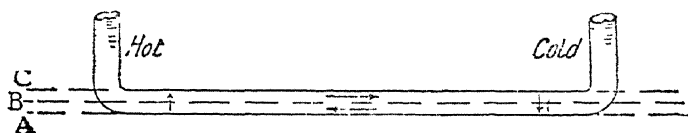


FIG 33

Regnault devised two methods, by which these errors are obviated, and the second one will now be described. It is probably the more accurate of the two.

The apparatus consists of two pieces of glass tubing, ABCD and EFGH, joined by a flexible iron tube to allow them to expand independently (Fig 34). The axes of the portions CB and GF are kept accurately in the same horizontal plane and the whole system of tubing is filled with mercury. The vertical arm CD is surrounded with an oil-bath and the portions EF, AB, and HG are jacketed with cold-water baths fed from a common supply. When equilibrium is attained the various heights indicated on the diagram and their corresponding temperatures are measured.

The calculation of the coefficient of expansion of mercury depends on the fact that the pressures at A and H are equal and so the pressure differences between A and D and

H and D are also equal. If ρ_0 , ρ_1 , ρ_2 , and ρ_3 are the density of mercury at temperatures 0°C , t_1 , t_2 , and t_3 respectively, we have

$$h_2\rho_1 + H_t\rho_3 = h_1\rho_1 + H_0\rho_1 + h_3\rho_2$$

But $\rho_0 = \rho_1(1 + \alpha t_1) = \rho_2(1 + \alpha t_2) = \rho_3(1 + \alpha t_3)$,

$$\therefore \rho_1 = \frac{\rho_0}{1 + \alpha t_1}, \text{ etc}$$

Substituting these values of ρ_1 , ρ_2 , and ρ_3 in the above equation, we have

$$\frac{h_2}{1 + \alpha t_1} + \frac{H_t}{1 + \alpha t_3} = \frac{h_1}{1 + \alpha t_1} + \frac{H_0}{1 + \alpha t_1} + \frac{h_3}{1 + \alpha t_2} \quad (31)$$

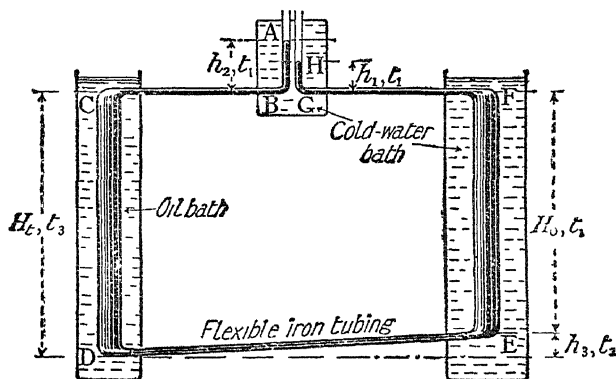


FIG. 34.

All the quantities except α in this equation have been measured, the only one about which there is any uncertainty being t_2 , the mean temperature of the mercury in the flexible iron tube. As the term involving this only contributes a very small quantity to the final result, an approximate value of it suffices. So equation (31) yields an accurate value of α , the coefficient of absolute expansion of mercury. It may be pointed out that this method eliminates both of the errors of Dulong and Petit's experiments, since the mercury columns are completely enclosed by their

respective constant temperature baths and the two mercury surfaces are at the same temperature

38. The Anomalous Expansion of Water.—The coefficient of expansion of a number of common liquids is given in Table V. Really accurate experiments show that no liquid expands uniformly, but the deviations are so marked in the case of water that ordinary laboratory experiments will detect them. The expansion of water is of interest in itself, but it is also of considerable importance as the unit of mass, the gram, was originally defined to be the mass of 1 c.c. of water at the temperature of its maximum density. We shall first consider a simple laboratory experiment which shows that water contracts from

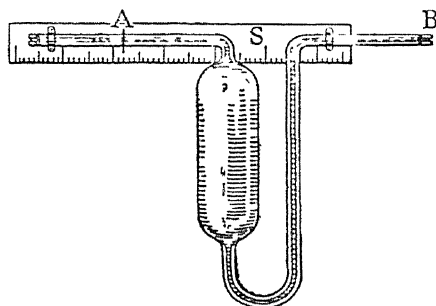


FIG 35 —A pycnometer

0°C to 4°C and then expands with further rise of temperature. A pycnometer of fused silica, whose expansion is negligible, is filled with air-free water (Fig 35) and mounted on a stand, to which are attached a stirrer and a thermometer reading to $\frac{1}{100}^{\circ}\text{C}$. The whole apparatus is immersed in a water-bath

at 10°C . and the pycnometer is tilted so that the water just comes to B, the other meniscus being a little way beyond the mark A. The water-bath is well stirred, the thermometer is read and the distance from the water meniscus to A is measured by the scale S attached to the pycnometer. A little ice is added to the water-bath, the stirring being continued, and when the temperature is stationary once more the distance of the water meniscus from A is again read. This is continued until the temperature reaches 0°C , readings being taken every two degrees or even more frequently round and about the temperature of maximum density. The same readings are now taken while the temperature is being raised to its original value and a graph of mean distance of the water

meniscus from A against temperature is plotted (Fig 36) It shows quite clearly that the volume of the water decreases as it is cooled until 4°C , when further cooling causes an increase in volume. Water is quite unique among common substances in this respect, although molten bismuth exhibits the same effect above its melting-point. The above experiment can

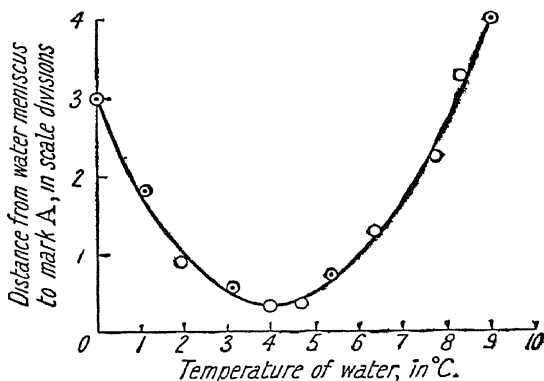


FIG. 36 —The expansion of water

be modified so as to give the coefficient of expansion of water, but the more important problem is to find as accurately as possible the temperature of maximum density

Two of the many experiments devised for this purpose will now be described

39. Hope's Experiment on the Maximum Density of Water.

—A tall beaker is filled with cold water and surrounded with a circular trough of ice at its middle point (Fig 37). The temperature of the water is measured at convenient intervals by two thermometers A and B and the readings are plotted on a graph as shown in Fig 38. The interpretation of this graph is as follows: the

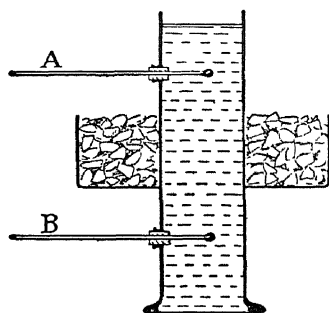


FIG 37 —Hope's apparatus for the maximum density of water

ice cools the water at its own level by conduction, thus making it heavier than the water underneath and causing it to sink. The initial rapid fall in the temperature

registered by B is due to the flow of heat away from it by convection, which continues until the water in the lower half of the beaker has reached the temperature of its maximum density. It then ceases because further cooling makes the water at the level of the ice less dense than that below. Therefore the reading of the thermometer B will remain constant at the temperature of the maximum density until such time as the water above becomes colder, when heat will slowly be taken from B by conduction. Meanwhile the initial cooling of A, due solely to conduction, is replaced by a more rapid drop in temperature due to convection, which sets in as soon as the density of the water round A becomes greater than

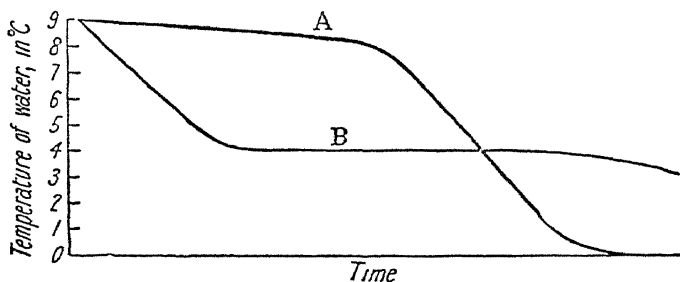


FIG 38 —Graph of thermometer readings in Hope's experiment

that at the level of the ice. The temperature of A then falls rapidly to zero and ice begins to form on the top of the water. The experiment gave 4.0°C as the temperature of the maximum density of water. It is interesting to observe that this anomalous behaviour of water is the reason why a pond freezes from the top downwards, if it behaved in the normal way we should not get any skating until the pond was frozen practically solid, which would seldom occur in this country!

40. The Method of Joule and Playfair.—The apparatus consists of two tall iron cylinders joined at the bottom by a tube fitted with a tap T and at the top by a trough which can be closed with a slide (Fig 39). The tanks are filled with hot and cold water at temperatures close to

and about equidistant from that of maximum density. The tap is closed and the slide is inserted in the trough, the water in each tank is well stirred and its temperature is noted. The tanks are then put into communication by opening the tap and removing the slide, and any flow is detected by putting a glass float in the trough and observing its motion. Let us suppose that the float indicates a flow from the hot to the cold tank in the trough and therefore from the cold to the hot through the tap. This means that the cold water is denser than the hot and that its temperature is more removed from that of maximum density than is the temperature of the hot water, assuming that the temperature density curve is symmetrical about the temperature of maximum density. Thus the mean temperature of the hot and cold water is less than that of maximum density and if the flow is in the opposite direction it will be greater. If no flow occurs, the mean temperature is equal to the temperature of maximum density. It is impossible to obtain this ideal result in practice, and so the velocity of flow is measured for various mean temperatures and a graph is drawn relating these two quantities. The mean temperature corresponding to zero flow is read from it and this is the required temperature. The result obtained by Joule and Playfair was 3.95°C , and this is regarded as the most accurate value of the temperature of the maximum density of water.

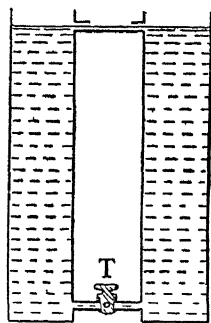


FIG 39 — Joule and Playfair's experiment

41. The Millilitre.—On the metric system the kilogram was originally defined to be the mass of 1 cubic decimetre of pure water at the temperature of its maximum density, in order to obtain a simple relation between the units of mass and volume. Soon after this definition had been agreed upon, certain French physicists were entrusted with the task of making a *standard kilogram of platinum*. Between 1821 and 1841 it was definitely established that

the standard did not agree with the above definition, and the question arose as to which should be adopted. It was finally decided to adhere to the standard, so the kilogram is now the mass of a cylinder of platinum carefully stored in Paris. But the simplicity of the original definition is destroyed by this choice, for the density of water is no longer 1 grm per c.c. at the temperature of its maximum density. The difference is small but it cannot be neglected in very accurate work, and is somewhat tiresome in volumetric work in Chemistry where the mass of water is deduced from its volume. The difficulty has been overcome by adopting a new definition of the litre, which was formerly either 1 cubic decimetre or the volume at the temperature of its maximum density of 1 kilogram of pure water. These two quantities are no longer the same, and the litre is now defined as "the volume of 1 kilogram of pure water at the temperature of its maximum density and under 1 standard atmosphere." On this definition 1 litre = 1000.028 c.c. The litre and the millilitre are now being widely adopted as the units of volume in chemical work, and many flasks, burettes, etc., are being calibrated in them. The maximum density of water is, of course, 1 grm per millilitre and the old simplicity is restored. Many tables of physical constants are already beginning to give densities in grm per ml.

TABLE V—THE COEFFICIENT OF EXPANSION OF LIQUIDS

Liquid	Coefficient of Expansion per °C $\times 10^4$
Mercury . . .	1.82
Ethyl alcohol . . .	11.0
Aniline . . .	8.5
Glycerine . . .	5.3
Turpentine . . .	9.4
Water 5° C to 10° C	0.53
20° C to 40° C	3.02
60° C to 80° C .	5.87

EXAMPLES ON CHAPTER IV

1 Prove that a hollow vessel expands as if it were a solid of the same shape, constructed of the same material as the envelope

A density bottle has a volume of 25.00 c.c. at 15° C and is full of mercury at the same temperature. What mass of mercury will be expelled from the bottle by heating it to 100° C.? The density of mercury at 0° C is 13.6 gm per c.c., its coefficient of expansion is 0.000182 per °C, and the coefficient of cubical expansion of the material of the density bottle is 0.000025 per °C

2 1 c.c. of glycerine at 0° C expands 0.00053 c.c. for each °C rise in temperature. If a given mass of glycerine has a volume of 100 c.c. at 30.0° C, calculate its volume at 150.0° C, (a) assuming only the above coefficient of expansion, (b) assuming that 1 c.c. of glycerine at 30.0° C also expands 0.00053 c.c. per °C rise in temperature. Find the percentage error introduced into the calculated volume at 150° C by the assumption made in the second case

3 Explain the connection between the coefficient of thermal expansion of a liquid and the variation of its density with temperature

Find the mass of mercury which must be introduced into a glass bulb of 20 c.c. capacity in order to make the volume of the unoccupied space in the bulb constant between 20° C and 100° C. The linear expansion of glass may be taken to be 8×10^{-6} per °C, while the densities of mercury at 20° C and 100° C are 13.546 and 13.352 gm per c.c. respectively (O and C)

4 What do you understand by the statement "The mean coefficient of expansion of mercury is 182×10^{-6} per °C"?

The density of mercury at 20° C is 13.55 gm per c.c. At what higher temperature will this figure be in error by 1 per cent? (N U J B)

5 The density of water at 15° C is 0.9991 gm per c.c. and its mean coefficient of absolute expansion from 15° C to 90° C is 0.00040 per °C. The corresponding quantities for aniline are 1.023 gm per c.c. and 0.00085 per °C. Find at what temperature a drop of aniline will float totally immersed in water

6 Describe the weight thermometer experiment for the determination of the coefficient of expansion of a liquid

When a glass weight thermometer filled with mercury at 0° C is heated to 100° C 7.785 gm of mercury overflow and 450.0 gm remain in the thermometer. Using glycerine in place of mercury the corresponding figures are 2.173 gm.

and 41.00 grm. The coefficient of expansion of mercury is 0.000183 per $^{\circ}\text{C}$. Determine (a) the coefficient of linear expansion of the glass, (b) the coefficient of volume expansion of the glycerine (*N U J B*)

7 Distinguish between the absolute and relative expansion of a liquid, and describe how you would determine the relative expansion of mercury in glass. Show how the coefficient is calculated from the measurements made (*O and C*)

8 A sinker of weight W_0 has an apparent weight W_1 when weighed in a liquid at a temperature t_1 and W_2 when weighed in the same liquid at a temperature t_2 . The coefficient of cubical expansion of the material of the sinker is β . What is that of the liquid? (*O and C*)

9 Explain the difference between the coefficients of absolute and apparent expansion of a liquid and find the relation between them

Why does the balancing of a hot against a cold column eliminate the expansion of the vessel? If the cold column at 4°C is 60 cm high and the hot column at 95°C is $\frac{1}{2}$ cm higher, what is the coefficient of absolute expansion of the liquid?

10 Describe a method of finding the coefficient of absolute expansion of a liquid

Show that the coefficient of apparent expansion of a liquid is very nearly equal to the difference between the coefficient of absolute expansion of the liquid and the coefficient of cubical expansion of the material of the containing vessel (*Camb Schol*)

11 Give a critical discussion of Regnault's method of finding the coefficient of absolute expansion of mercury

12 If λ is the coefficient of linear expansion of a solid, explain carefully why 3λ may be used as the coefficient of cubical expansion

The height of a mercury barometer read with a steel scale is 754 millimetres at 20°C . What will it read at 0°C ?

(Coefficient of linear expansion of steel 0.000012 per $^{\circ}\text{C}$)

(Coefficient of cubical expansion of mercury 0.000182 per $^{\circ}\text{C}$) (*O and C*)

13 Derive the relation between H_0 , H_t , and α , where H_0 is the height of a mercury barometer at 0°C , H_t its height at $t^{\circ}\text{C}$ and α is the coefficient of absolute expansion of mercury

The height of the barometer measured by a steel scale on a day when the temperature is 11.0°C is 75.347 cm. Find the height of the barometer in cm of mercury at 0°C , if the scale reads correctly at this temperature. (Use the coefficients of expansion given in the previous question)

14 The pressure of the atmosphere at a given place and at a certain time is one million dynes per sq cm. Calculate the height, H , of a mercury barometer at that place and time if the temperature is 25°C and the height is measured with a steel scale correct at 15°C . Use the values of the coefficients given in question 12, and take the value of g as $981.3\text{ cm per sec}^2$ and the density of mercury at 0°C as 13.59 gm per cc .

15 The expansion of water is observed by using a glass bulb (coefficient of volume expansion $0.000025\text{ per }^{\circ}\text{C}$) sealed on to a capillary tube. The volume of the water at 0°C is 10 cc and 1 cm length of the bore has a volume of 1 cmm . Taking the level of the meniscus at 0°C as zero the readings are

Temp $^{\circ}\text{C}$.	2	4	6	8	10	12	14
Reading cm	—	1.5	2.3	2.5	2.0	1.1	0.4	2.5

Plot curves showing (a) the apparent and (b) the true change in the volume of the water as its temperature is changed. Plot temperatures as abscissæ (scale $1\text{ in} = 2^{\circ}\text{C}$) and changes in volume as ordinates (scale $1\text{ in} = 2\text{ cmm}$). Ignore all effects due to the expansion of the capillary tube.

Using data obtained from curve (b), find the average increase in volume per unit volume at 0°C per degree rise in temperature for the range 5°C to 10°C . (*NUJB*)

16 Give a critical account of the experiments which have been made to find the temperature of the maximum density of water. Discuss their bearing on the units of mass and volume.

17 Devise a method of measuring the coefficient of cubical expansion of a solid of which only a small quantity is available and which cannot be polished.

CHAPTER V

THE EXPANSION OF GASES

42 **Boyle's Law.**—Unlike solids and liquids gases have no size, that is, their volume can be altered by varying the pressure as well as the temperature. It follows that a gas possesses three variables, *pressure*, *volume*, and *temperature*, which are presumably related to one another by an equation which can be found by keeping each variable

constant in turn and investigating experimentally the relation between the other two

We will consider in the first place the relation between the pressure and volume of a gas at constant temperature. We shall not describe the well-known experiment by which this relation is investigated, since it is adequately treated in the elementary text-books on the subject. But it is important to consider the nature of the results obtained from the experiment. These show that, within the limits of experimental error, the product of the pressure and volume of the gas is constant or a graph of the pressure and the reciprocal of the volume is a straight line through the origin. We may say then that "the volume of a given mass of gas is inversely proportional to its pressure provided that the temperature is kept constant." That is

$$pv = \text{constant} \quad . \quad . \quad . \quad (32)$$

at constant temperature. This is called **Boyle's law** after Robert Boyle, who discovered it in 1662. Later investigation showed that it is true for any gas remote from its point of liquefaction. It is necessary to emphasise here the phrase "within the limits of experimental error." This means that the value of the product of the pressure and volume shows no *systematic* variation, no steady increase or decrease as the pressure increases. There are variations, but they are irregular; sometimes the product increases and sometimes it decreases as the pressure increases. Expressed in terms of the graph, the points are evenly distributed about the straight line through the origin, but they do not invariably lie on it. So it is correct to infer from our results that "the volume of a given mass of gas is inversely proportional to the pressure" provided that we bear in mind that this is not the last word, for our conclusion stands open to modification if the experiments are repeated more accurately or over a wider range of pressure, so that deviations from it, too small to be detected by the above experiments, may be revealed if they exist. As we have noticed before (Art. 22) science is a *series of approximations to the truth*, and all experimental laws and theories based on them are liable to revision, or even rejection, in the light of more accurate work or new facts.

43. The Expansion of a Gas at Constant Pressure.—

When a gas is heated at constant pressure experiment shows that it expands uniformly, and **the coefficient of expansion** of a gas is the increase in volume per unit rise in temperature of the mass of gas occupying unit volume at 0°C , the pressure being constant. The above definition is not complete until we have chosen our scale of temperature, we shall use the constant volume hydrogen scale as defined in Art 6, and all thermometers used in the experiments described in this chapter are to be regarded as calibrated according to that scale.

The reader is referred to the elementary text-books for an account of the ordinary experiments for measuring the coefficient of expansion of gases. The results obtained are at once striking and simple. It is found that all the so-called permanent gases, such as air, hydrogen, and nitrogen, which are remote from the liquefying point under the conditions of this experiment, have the same coefficient of expansion, $\frac{1}{273}$ per $^{\circ}\text{C}$. That is, a mass of any of these gases occupying 273 c.c. at 0°C shows an increase in volume of 1 c.c. for each $^{\circ}\text{C}$ rise in temperature. The striking feature of this result is that all the permanent gases have the same coefficient of expansion. There may be small differences which more accurate experiments will reveal, but in any case the above method is accurate enough to show that there is no such variation in the coefficient of expansion of different gases as exists in the case of solids and liquids. This is evidently a most significant fact; its chemical counterpart is to be found in Avogadro's hypothesis, and any theory of gases must account for these properties common to them all when remote from the point of liquefaction. The above results may be summarised in the statement known as **Charles' law**: "that mass of any gas which has a volume of 273 units at 0°C expands by 1 unit for each $^{\circ}\text{C}$. rise in temperature, provided that the pressure remains constant." Mathematically, if a volume V_0 of the gas at 0°C expands at constant pressure to a volume V_t at $t^{\circ}\text{C}$, we have

$$V_t = V_0 (1 + \alpha t) \quad . \quad . \quad . \quad (33)$$

at constant pressure, where α = the coefficient of expansion of the gas and is $\frac{1}{273}$ per $^{\circ}\text{C}$ for all gases.

It will be as well to point out here that the above equation cannot be used to calculate directly the volume of a gas at some temperature $t^{\circ}\text{C}$ from its initial volume at a temperature other than 0°C . Suppose we have 273 c.c. of a gas at 0°C , the volume at 50°C and 100°C is 323 c.c. and 373 c.c. respectively. If we try to calculate the volume at 100°C given that at 50°C , assuming the coefficient of expansion at 50°C to be still $\frac{1}{273}$ per $^{\circ}\text{C}$, we get

$$\begin{aligned}\text{the volume of the gas at } 100^{\circ}\text{C} &= 273 \left(1 + \frac{1}{273} \cdot 50\right) \\ &= 322.2 \text{ c.c.}\end{aligned}$$

The difference between this and the true volume, 373 c.c., is much too great to be neglected, and so the assumption that the coefficient of the gas at 50°C is still $\frac{1}{273}$ per $^{\circ}\text{C}$ is not justified. The volume at 100°C must be worked out by finding the volume at 0°C from the equation

$$323 = V_0 \left(1 + \frac{1}{273} \cdot 50\right)$$

and then using this value of V_0 to calculate the volume, V_{100} , at 100°C from the equation

$$V_{100} = V_0 \left(1 + \frac{1}{273} \cdot 100\right).$$

It will be shown later on, however, that there is a simpler way of performing these calculations (Art 47)

44. Regnault's Experiments.

Regnault set himself the task of devising really accurate experiments to test the uniformity of the expansion of gases and to find the coefficient of expansion of the various gases as accurately as possible. His apparatus, which is illustrated diagrammatically in Fig 40, consists of a bulb B joined by a capillary tube to a mercury manometer DEFG which is immersed in a constant temperature water-bath. The bulb is alternately exhausted and filled

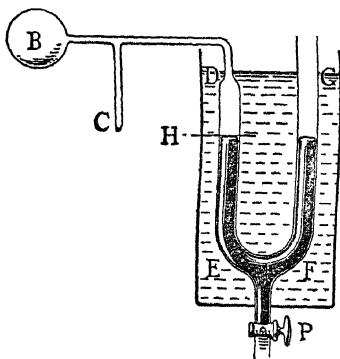


FIG 40—Regnault's apparatus for finding the coefficient of expansion of gases

with dry air several times in order to remove all traces of moisture adhering to it and to ensure that the air is quite dry. The capillary tube C is then sealed off. After the bulb has been immersed in melting ice for some time, the levels of the mercury in the manometer are adjusted to be the same and the reading of the mercury at H is noted. The bulb is then placed in a water-bath, whose temperature is read by a suitable thermometer, and the air expands forcing the mercury down in DE and up in FG. The pressure of the air is restored to its original value by letting out mercury through the tap P until the levels are once more equal and the reading of the mercury in DE is again noted. These readings are continued at intervals of 10°C , the final set of measurements being made with the bulb immersed in steam. The readings are repeated at the same temperatures while the gas is cooling down again, and the mean value of the readings obtained when it is heating up and cooling down is used in working out the results. The experiment can, of course, be used for investigating the expansion of other gases besides air.

In order to see if the gas expands uniformly, Regnault made use of the fact that non-uniformity of expansion will show itself by the variation of the coefficient of expansion at 0°C calculated for different ranges of temperature. Suppose, for the sake of argument, that 273 c.c. of a gas at 0°C expand 50 c.c. in being heated from 0°C to 50°C and a further 50 c.c. in being heated from 50°C to 100°C , that is, its expansion is uniform. Then the coefficient of expansion between 0°C and 50°C is $\frac{1}{273}$ per $^{\circ}\text{C}$, which is equal to that between 0°C and 100°C . But if the gas expands 50 c.c. in being heated from 0°C to 50°C and 60 c.c. in being heated from 50°C to 100°C , then the coefficient of expansion between 0°C and 50°C is still $\frac{1}{273}$, whereas between 0°C and 100°C it is $\frac{110}{273 \times 100} = \frac{1}{248}$. This quantity is called the **mean coefficient of expansion between 0°C and $t^{\circ}\text{C}$** and is given in general by the expression $\frac{V_t - V_0}{V_0 t}$ where V_0 and V_t are the volumes of the gas at 0°C and $t^{\circ}\text{C}$ respectively. If the mean coefficient of expansion

between 0°C . and $t^{\circ}\text{C}$ varies with the temperature t then the gas does not expand uniformly. Regnault calculated this quantity from his readings in the following way. Let V , v_1 , and v_2 be the volume of the bulb, capillary tube, and the limb DE of the manometer up to the mark H respectively. These volumes have to be found before starting the actual experiment and the limb DE must also be calibrated. Assuming that the bulb, capillary tube, and manometer are at the same temperature as one another, the volume of the gas at $0^{\circ}\text{C} = V + v_1 + v_2$. When the gas is heated to $t^{\circ}\text{C}$, let the volume of the manometer occupied by it increase to v'_2 . Then the volume of the gas at $t^{\circ}\text{C} = V + v_1 + v'_2$. The mean coefficient of expansion between 0°C . and $t^{\circ}\text{C}$ is

$$\frac{(V + v_1 + v'_2) - (V + v_1 + v_2)}{(V + v_1 + v_2)t}$$

$$= \frac{v'_2 - v_2}{(V + v_1 + v_2)t}$$

The equation that Regnault used was actually more complicated than this because he corrected for the following errors:

(a) The portions of the gas in the bulb, capillary tube, and manometer are all at different temperatures

(b) The volume of the bulb, etc., changes owing to the expansion of the glass

(c) The pressure may not be quite the same at the initial and final temperatures owing to the difficulty of getting the mercury levels exactly equal.

Regnault found that all gases show small departures from uniform expansion. He then proceeded to calculate the mean coefficient of expansion between 0°C and 100°C from the readings taken when the bulb was in melting ice and steam and obtained the following results:

Air	0 003671
Hydrogen	0 003661
Carbon monoxide	0 003669
Carbon dioxide	0 003710

It will be noticed that none of the gases has a coefficient of expansion of precisely $\frac{1}{273} = 0.003662$ and that the values

for the various gases differ slightly from one another, which is just what would be expected

45. The Increase in Pressure at Constant Volume.

We can now pass on to the third type of change to which a gas can be subjected, in which a rise in temperature while the volume is kept constant produces an increase in pressure. **The coefficient of increase in pressure at constant volume of a gas, or its pressure coefficient,** is defined as the increase in pressure per unit rise in temperature of a mass of the gas having a unit pressure at 0°C , the volume being constant. It can be found to a first approximation (that is, to an accuracy of 1 per cent) by using Joly's apparatus, which is illustrated in Fig 4. The gas can be heated by immersing the bulb in a water-bath, whose temperature is measured by a thermometer graduated on the constant volume hydrogen scale. Otherwise the apparatus is just the same as the rough constant volume gas thermometer described in Art 4 and the volume of the gas is kept constant and its pressure is measured as described there. Readings of pressure and temperature are taken at intervals of 10°C between 0°C . and 100°C , both when the gas is being heated up and is cooling down again, and a graph of the mean of these two readings of the pressure is plotted against the temperature. From this graph the increase in pressure per $^{\circ}\text{C}$ rise in temperature, the pressure at 0°C , and so the pressure coefficient can easily be calculated. The results of this preliminary survey are just what we should expect. It is found that the pressure of all gases increases uniformly with temperature, and that their pressure coefficient is $\frac{1}{273}$ per $^{\circ}\text{C}$. The fact that all gases have the same pressure coefficient, which is numerically equal to their coefficient of expansion, is a consequence of Boyle's law as will be shown below (Art. 46). We may express these results mathematically by saying that if the pressure p_0 of a given mass of gas at 0°C increases to p_t at $t^{\circ}\text{C}$, the volume being constant, then

$$p_t = p_0 (1 + \beta t) \quad . \quad . \quad . \quad (34)$$

at constant volume, where β = the pressure coefficient of the gas

A more accurate determination of the pressure coefficient of gases, as was undertaken by Regnault, can be made with an apparatus such as Harker and Chappuis' constant volume gas thermometer (Fig 5). The bulb is heated to various temperatures by immersing it in a suitable bath, and the volume of the gas is kept constant and its pressure is measured as described in Art 5. The temperature is measured by an independent thermometer. It is necessary to make corrections both for the change in volume of the gas owing to the expansion of the bulb and for the fact that the gas in the "dead space" is not at the same temperature as that in the bulb. That is, we must find from the measured pressure what the pressure of the gas would be if the bulb did not expand and the gas in the "dead space" were at the same temperature as that in the bulb. In experiments on hydrogen no measurement of temperature is necessary, since the increase in pressure is uniform because we are using the constant volume hydrogen scale of temperature. It is merely necessary to measure the pressure of the gas when the bulb is at 0°C (in melting ice) and 100°C . (in steam) in order to find the pressure coefficient. With the exception of hydrogen it is found that the pressure at constant volume of a gas does not quite increase uniformly with temperature. When the mean pressure coefficient between 0°C and 100°C is calculated, it is found that the values for different gases show slight differences among one another and in no case is it equal to $\frac{1}{273}$. The results for a few gases are appended:

Air	0.003674
Hydrogen	0.003663
Nitrogen	0.003675
Carbon dioxide	0.003725

A comparison of the coefficient of expansion of a gas with its pressure coefficient shows that the two are never exactly equal, which indicates that gases do not obey Boyle's law strictly, a possibility which we have already noticed. It is essential to obtain direct evidence of these deviations from Boyle's law, and experiments with this aim will be described later (Art 112). It may also be pointed out that it is the most easily condensible gases, such as carbon dioxide,

which show the greatest departure from the results for the permanent gases, which are in such close agreement with one another. This suggests an investigation of the permanent gases at low temperatures in order to see if there is any radical difference between them and carbon dioxide or if they will follow its behaviour under such conditions. An account of this investigation is given in Chapter X on the relation between the liquid and gaseous states.

46. The Ideal Gas Scale of Temperature.—Let us imagine that we have a gas which obeys Boyle's law strictly, and that we decide to measure temperature on the constant volume scale of this gas. Then it obeys the following two equations:

$$pv = \text{constant} \quad . \quad . \quad . \quad (35)$$

at constant temperature,

$$p = p_0 (1 + bt) \quad . \quad . \quad . \quad (36)$$

at constant volume, where b = the pressure coefficient of the gas. We shall now show that it follows from these equations that the coefficient of expansion of the gas is also b . Suppose a given mass of the gas has a volume v_0 and pressure p_0 at 0°C . By increasing the temperature to $t^\circ \text{C}$ at constant volume the pressure becomes p given by equation (36). If the pressure is now restored to its original value, p_0 , while the temperature is kept constant, the new volume v is given by

$$p_0 v_0 = p v = p_0 (1 + bt) v$$

since the gas obeys Boyle's law.

Substituting the value of p from equation (36) in this equation, we have

$$\begin{aligned} p_0 v_0 &= p_0 (1 + bt) v \\ v &= v_0 (1 + bt) \quad . \quad . \quad . \quad (37) \end{aligned}$$

at constant pressure. As v is the volume at $t^\circ \text{C}$ of the mass of gas having a volume v_0 at 0°C , the pressure being p_0 , equation (37) shows that the gas expands uniformly with a coefficient of expansion exactly equal to its pressure coefficient. This has already been found to be approximately true of all gases (Art 45) and we see

that it is because they obey Boyle's law. Such a gas is called the **ideal gas** because of its ideally simple properties and because it represents the behaviour of all actual gases to a first approximation. Now let us base a scale of temperature on the increase in volume of the ideal gas at constant pressure and call it the constant pressure ideal gas scale. Then it agrees with the constant volume ideal gas scale, since the volume of the ideal gas at constant pressure varies uniformly with temperature measured on the constant volume ideal gas scale (see Fig. 10 and Art. 8). In future either of these two scales will be referred to indiscriminately as the ideal gas scale of temperature. Now it is found by experiment that as the pressure decreases the behaviour of all gases becomes more and more nearly identical with that of the ideal gas and can be made as close as we like by making the pressure low enough. *The ideal gas, in fact, expresses the behaviour common to all gases at infinitely low pressure, when they all obey Boyle's law strictly and have the same coefficient of expansion and pressure coefficient, which is found by experiment to be $\frac{1}{273 \cdot 20}$ per ° C.* It follows from these facts that the ideal gas scale of temperature is a closer approach than the constant volume hydrogen scale to the non-arbitrary scale, the necessity for which was stressed at the end of Chapter I. Its claim to this position is founded on the fact that it is based, not on the properties of *one* gas, but on those common to *all* gases at infinitely low pressure. In other words, it is less arbitrary than the hydrogen scale because it is not dependent on the properties of one particular material substance, such as the gas hydrogen. This scale would be of no practical use unless it was possible to determine the correction which must be added to a temperature measured on, say, the constant volume hydrogen scale as defined in Art. 6 to obtain the corresponding temperature on the ideal gas scale, for it is hardly necessary to point out that the ideal gas cannot be realised in practice, and so temperatures cannot be measured directly on this scale. The correction can be calculated from the Joule-Kelvin effect (Art. 115), which measures in numbers the deviation of a gas from the ideal gas, but the details are

beyond the scope of this book. It will be assumed in future that all temperatures are measured on the ideal gas scale unless some other scale is explicitly specified.

The three equations (35), (36), and (37), each relating two out of the three variables of the gas, can be replaced by the following equation relating all the three

$$pv = p_0 v_0 (1 + bt) \quad . \quad . \quad . \quad (38)$$

It is easy to show that this equation expresses in itself the three previous ones. If the volume is kept constant, $v = v_0$, and it reduces to equation (36), if the pressure is kept constant, $p = p_0$, and it reduces to equation (37). If the temperature is constant ($1 + bt$) is constant, and when the volume v_0 of a given mass of the gas at 0°C is decided upon its pressure p_0 is thereby fixed, so $p_0 v_0$ and therefore $p_0 v_0 (1 + bt)$ is constant, that is, the equation reduces to equation (35). It is important to bear in mind that these equations are only true if the mass of gas is constant.

47. Absolute Temperatures.—Let us return for a moment to the constant volume hydrogen scale, which can be represented by the equation

$$p = p_0 (1 + \beta t),$$

where β = the pressure coefficient for hydrogen when p_0 is 1 metre of mercury

$$\begin{aligned} \therefore p &= p_0 \beta \left(\frac{1}{\beta} + t \right), \\ \therefore p &= kT \quad . \quad . \quad . \quad (39) \end{aligned}$$

where $k = p_0 \beta$, a constant,

$$T = \frac{1}{\beta} + t \quad . \quad . \quad . \quad (40)$$

and is called the **absolute temperature** corresponding to $t^\circ \text{C}$. This absolute temperature T is still a temperature on the constant volume hydrogen scale, only it is measured not from the Centigrade zero, which is purely arbitrary, but from the **absolute zero**, which is given in $^\circ \text{C}$. by the equation

$$\begin{aligned} 0 &= \frac{1}{\beta} + t, \\ \therefore t &= -\frac{1}{\beta}. \end{aligned}$$

That is, the absolute zero is $\frac{1}{\beta}^{\circ}$ below the Centigrade zero

It is called the absolute zero, because the pressure of hydrogen at constant volume would have decreased to nothing at this temperature provided that the gas did not liquefy. It is impossible to conceive of the gas exerting a negative pressure, and so it is reasonable to suppose that this may be the lowest temperature which can be reached, therefore our zero is absolute, not just a convenient fixed temperature arbitrarily selected largely on account of its practical convenience. It may be emphasised here that absolute temperatures are not measured on a new scale but merely from a new zero of the original scale.

What can be done for the constant volume hydrogen scale can also be done for the ideal gas scale. From equation (38) we have

$$pv = p_0 v_0 \left(\frac{1}{\beta} + t \right)$$

Putting $p_0 v_0 \beta = C$, a constant, we have

$$pv = CT \quad . \quad . \quad . \quad . \quad (41)$$

where

$$T = \frac{1}{\beta} + t$$

and is the absolute temperature corresponding to t° C. Equation (41) is called the **gas equation**, because it represents approximately the behaviour of all gases under ordinary conditions. It is also the equation which represents precisely the limiting behaviour of all gases at infinitely small pressure. Therefore at infinitely low pressure the volume at constant pressure and the pressure at constant volume of all gases will become zero at 0° A. The fact that all gases will have either zero volume or zero pressure at this temperature makes it most probable that this is the lowest temperature which can be reached. How far this prediction has been verified will be seen in Chapter XI, which deals with the liquefaction of gases and the production of low temperatures. But we may notice here that the notion of an absolute zero is a very reasonable one, since it is the temperature at which all the heat has been taken out of the body, after which it is

impossible to make it any colder. It is interesting to notice that since $b = \frac{1}{273 \cdot 20}$, the temperature of the melting-point of ice $= 273 \cdot 20^\circ \text{ A}$ on the ideal gas scale. For hydrogen $\beta = \frac{1}{273 \cdot 03}$, so the melting point of ice $= 273 \cdot 03^\circ \text{ A}$ on the constant volume hydrogen scale. It is seen that the two scales agree very closely, and that is the other reason referred to in Art 8 for choosing the constant volume hydrogen scale as the arbitrary scale, while a non-arbitrary one was being sought. It was already known that hydrogen showed the least departure from Boyle's law, and so it was thought that it might show the least difference of all gas scales from the non-arbitrary scale when it was found.

The gas equation may be used in converting the volume of a gas at one temperature and pressure into that at another, as is frequently necessary in Chemistry in standardising gas volumes. If 50 c.c. of hydrogen are collected at 10° C and 74.5 cm. pressure, what is its volume at N.T.P. (0° C and 76 cm. pressure)? It is sufficiently accurate in such calculations to take $0^\circ \text{ C} = 273^\circ \text{ A}$.

From equation (41)

$$\frac{pv}{T} = C, \text{ a constant}$$

If v = the volume of the hydrogen at N.T.P.,

$$\therefore \frac{76v}{273} = \frac{74.5 \times 50.0}{283},$$

whence $v = 47.3 \text{ c.c.}$

48. The Gas Constant.—This chapter will be concluded with three calculations of the constant C in equation (41), which will serve to illustrate that the gas equation is only true for constant mass of the gas and that the constant C is different for different masses of the same gas and for the same mass of different gases. It is really more in the nature of a *parameter* than a constant.

To calculate C for 1 gram of oxygen, we use the fact that the volume of 1 gram of oxygen at N.T.P. is 699.9 c.c. We must express the pressure in dynes per sq. cm. to get the

constant in ergs per gram per degree, the dimensions of $p\nu$ being the same as those of energy. The normal pressure is that exerted by a column of mercury 76 cm long at 0°C , at sea-level and 45° latitude, where $g = 980.6$ cm per sec per sec. The normal temperature is 0°C or 273.2°A

$$\begin{aligned}\therefore 76 \times 13.60 \times 980.6 \times 699.9 &= C \times 273.2, \\ \therefore C &= 2.60 \times 10^6 \text{ ergs per gram per degree}\end{aligned}$$

It can easily be seen that the value of C will be ten times as great for 10 gram of oxygen, since the volume at N.T.P. will be ten times as big, the other quantities remaining the same. Furthermore, the value will be different for 1 gram of hydrogen, say, since it occupies 11,130 c.c. at N.T.P. The value is given by

$$\begin{aligned}76 \times 13.60 \times 980.6 \times 11130 &= C \times 273.2, \\ C &= 4.13 \times 10^7 \text{ ergs per gram per degree.}\end{aligned}$$

Although its value is different for different gases, **the gas constant for unit mass** of a gas is of considerable importance and it will be denoted by the letter r in this book.

There is one other value for C which is very important, its value for **the gram-molecule** of a gas. By Avogadro's hypothesis, the volume occupied by the gram-molecule of all gases is the same at N.T.P. It follows at once that the constant C for the gram-molecule is the same for all gases. This universal constant will be denoted by the letter R throughout this book. Its value is easily calculated from the fact that the volume of the gram-molecule of any gas at N.T.P. is 22,410 c.c.

$$\begin{aligned}\therefore 76 \times 13.60 \times 980.6 \times 22410 &= R \times 273.2, \\ \therefore R &= 8.31 \times 10^7 \text{ ergs per gram molecule per degree.}\end{aligned}$$

EXAMPLES ON CHAPTER V

1. State very briefly and in general terms the plan which has been followed in attacking the problem of the relation between the volume, pressure, and temperature of gases. Discuss the results which have been obtained, and show how they have been classified into a single mathematical equation.

2 350 c.c. of argon are collected in a gas jar over water, the volume being read when the level of the water is the same inside and outside the jar. The temperature is 17°C and the height of the barometer is 75.7 cm. The vapour pressure of water at 17°C is 1.5 cm. Calculate the volume of the argon at N.T.P. (0°C and 76 cm pressure).

3 1 gram of oxygen occupies 701 c.c. at N.T.P. What volume will it occupy at the critical point (Art. 110) when its pressure is 58 atmospheres and its temperature is -117°C , assuming that it obeys Boyle's and Charles' laws right to this point?

4 The density of hydrogen at N.T.P. is 0.089 gm. per litre. Calculate its density at 25°C and 72.5 cm. pressure.

5 A volume of air is enclosed between the sealed end of a glass tube and a water index, the other end of the tube being open to the air. The length of the enclosed column is 10 cm. at a temperature of 17°C , the atmospheric pressure being 75 cm. of mercury. What will be the length of the column at 60°C , the atmospheric pressure remaining unaltered? The vapour pressure of water at 17°C and 60°C is 15 mm. and 150 mm. respectively. (*O. and C.*)

6 Describe a method of determining the coefficient of expansion of a gas at constant pressure, and point out any difficulties in connection with the experiment.

A quantity of air at 30°C and a pressure of 15 lb. per sq. inch is suddenly compressed into $\frac{1}{1.5}$ of its original volume. The pressure is then found to be 500 lb. per sq. inch. How will the temperature of the air alter, and why? Calculate the change in temperature. (*Oxford Schol.*)

7 Describe how you would determine the boiling point of a salt solution with a constant volume air thermometer.

In 1802 Dalton observed that 1000 volumes of air at 55°F . become 1321 volumes at 212°F ., the pressure being constant. Compare the value of the coefficient of expansion of air at constant pressure given by these observations with the ordinary text-book value.

8 Give a diagram only, appropriately labelled, showing the essential features of apparatus of a type used for measuring accurately the mean value of the coefficient of expansion of a gas maintained at constant pressure.

An air bubble rises from the bottom of a pond, where the temperature is 7°C ., to the surface 27 metres above, at which the temperature is 17°C . Find the relative diameters of the bubble in the two positions, assuming that the pressure at the pond surface is equal to that of a column of mercury of density 13.6 gm. per c.c. and 76 cm. in height. (*N.U.J.B.*)

9 State the laws which describe the physical changes which take place when heat is imparted to a gas, and draw diagrams of apparatus with which experiments could be made to verify these statements

On a day when the air temperature is 10°C , a barometer at ground level shows a reading of 76 cm of mercury. On taking the barometer to the bottom of a mine shaft, where the temperature is 27°C , the air pressure is found to have increased by 4 cm of mercury. What is the ratio of the density of the air at the bottom of the shaft to that of the air at the top? (*NUJB*)

10 Prove that, if a gas obeys Boyle's law strictly, its coefficient of expansion at constant pressure is exactly equal to its pressure coefficient

How did Regnault use this result to try to find out if actual gases do obey Boyle's law strictly? Give a short account of his experiments and the results he obtained

11 Explain clearly what is meant by an "ideal gas". Discuss the ideal gas scale of temperature

12 Describe experiments by which it can be shown that a perfect gas obeys the law

$$pv = RT$$

where p is the pressure in a volume v of gas at absolute temperature T , and R is a constant

A faulty barometer contains a little air in the space above the mercury. On a day when the mercury column in this barometer is 75.1 cm long the space above the mercury is 10 cm; the tube is then pushed down 6 cm into the reservoir and the mercury column is found to be 73.5 cm. Calculate the value of the atmospheric pressure. (*Oxford Schol*)

13 Calculate the gas constant for 1 grm of argon, given that the density of argon at N.T.P. is 1.795 grm per litre

CHAPTER VI

CHANGE OF STATE

49. Fusion.—The fundamental laws of fusion can be illustrated by a simple experiment in which a test-tube of distilled water is cooled by enclosing it in a freezing mixture, from which it is separated by an air space. The water is

constantly stirred to keep the whole of it at a uniform temperature, which is read every minute by a thermometer. When the temperature reaches 0°C crystals of ice at once begin to form at various places in the water *and the temperature ceases to fall*, provided that the mixture of ice and water is thoroughly stirred, until all the water has turned to ice. After that the temperature commences to fall once more and a cooling curve of these changes would be of the form shown in Fig 41. If the above sequence of changes is now reversed by replacing the freezing mixture with a warm water-bath, the temperature of the ice rises steadily until 0°C is once more reached, when it commences to melt at the surface and the temperature stops rising. The mixture of ice and water is well stirred *and the temperature remains at 0°C until all the ice has melted*, after which it begins to rise again. If a graph of temperature against time is plotted, it will be of exactly the same form as the cooling curve in Fig 41 and the horizontal portion of each would be located at the same temperature, which is called the melting point of the solid.

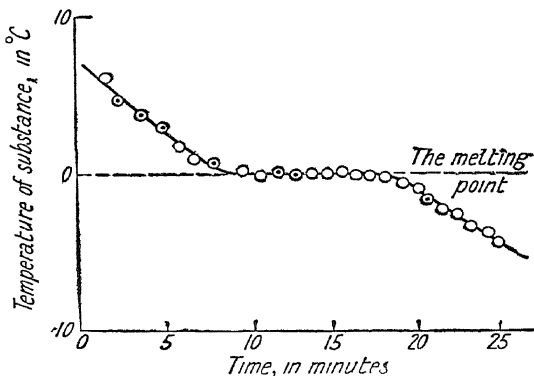


FIG 41 —The cooling curve for water.

A simple experiment of this kind demonstrates the laws of fusion which express the behaviour of all crystalline solids. There are two important laws which may be summed up in the following way

(a) A solid melts at a definite temperature, which coincides with that at which the liquid solidifies and is called the **melting point** of the solid

(b) Since the temperature of the solid remains the same

while it is melting, it follows that a considerable quantity of heat is absorbed. This is called latent heat, that is, hidden heat, because it does not manifest itself by the usual rise of temperature. An equal amount of heat is evolved when the liquid solidifies.

The quantitative definition of the latent heat of fusion of a solid and its experimental determination have been dealt with in Art 15 and will not receive any further consideration here.

It follows from the first law that a solid is unstable above, and a liquid below, the melting point. This temperature is the only one at which both the solid and

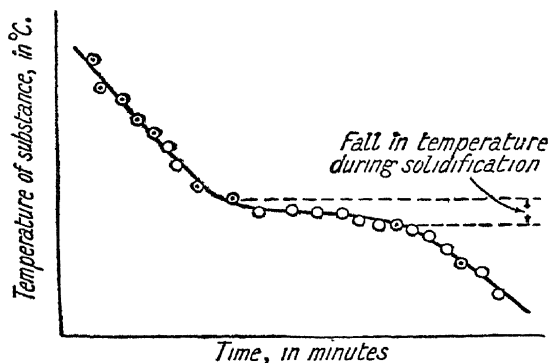


FIG 42 —The cooling curve of an amorphous solid

the liquid are stable, it is the only one at which they can exist together in equilibrium. Not only does the melting occur at a definite temperature, but the distinction between the solid and liquid states is just as sharply defined. When water freezes it does not become more and more viscous as it approaches 0°C , but remains quite fluid until that temperature is reached, when hard crystals of ice suddenly appear at various places. In the same way, when ice is heated it does not become more and more plastic as 0°C is approached, but remains quite hard until water is formed on the surface as soon as the melting point is reached.

The changes which accompany the melting of amorphous solids, such as iron, glass, and paraffin wax, are not so simple as those which have just been described. In the first place there is no definite temperature at which melting or solidification occurs. If a cooling curve for such a substance

is obtained, it will be of the form shown in Fig 42, in which a finite fall of temperature takes place during solidification. There is a similar lack of definiteness in the transition from the properties of the solid to those of the liquid. When a piece of glass is heated, for example, the whole of it becomes more and more plastic and gradually turns to a liquid which gets less and less viscous with rise of temperature. There is no abrupt change from a hard solid to a mobile liquid but a gradual transition from one to the other during which a substance is formed, whose properties are intermediate between those of a solid and a liquid. Contrast this with the melting of ice, in which a mobile liquid is formed at a definite temperature at the surface of the ice, the rest of which is quite hard and definitely a solid. The behaviour of amorphous solids may be due to the fact that we are dealing with a mixture of two or more substances, which would not solidify at a definite temperature, as will be explained below in connection with the fusion of alloys (Art 52).

There is always a change in volume when a solid melts. This effect is common both to crystalline and amorphous solids and can be shown in the following way. If a test-tube partly filled with distilled water is closed with a cork pierced with a narrow tube, the rest of the test-tube and some of the capillary tube being filled with turpentine or some other liquid which freezes well below 0°C , the turpentine at once rises up the tube when the water is turned to ice by plunging the test-tube in a freezing mixture. This shows that when water freezes an increase in volume takes place, which is confirmed by the fact that ice floats on water. This expansion is the source of a very considerable force if it is opposed and can be made to burst a steel bottle. It is, of course, the cause of the bursting of water pipes in frosty weather. Iron, bismuth, and antimony also expand on solidifying, and for that reason iron is specially suitable for making castings. In one method of printing the type is cast in a mould and an alloy of copper, antimony, and lead, which is used for the purpose, expands on solidifying and therefore fills up all the minute lines and crevices in the mould and reproduces it with the utmost precision. But the majority of substances contract on

solidifying, a good example being paraffin wax. The effect can easily be shown in this case by melting a few pieces in a test-tube; on cooling it under the tap the surface is seen to be concave, showing that the solid occupies less volume than the liquid from which it was formed.

Many experiments have been performed to find directly the volume of liquid formed from a given volume of the solid, but in many cases the simpler and more accurate way of determining this quantity would appear to be by deducing the volumes of unit mass of the solid and liquid from their respective densities at the melting point.

50. Surfusation.—If a test-tube of distilled water is cooled without stirring the water or disturbing it in any way, the temperature will be observed to fall three or four degrees below 0°C without any ice being formed. Then, for no apparent reason, ice crystals suddenly appear, and the temperature of the water is immediately raised to 0°C by the latent heat evolved. If the water is covered with a layer of oil to keep it free from dust, it can be kept at -12°C without solidification setting in. The water is said to be *surfused* when it is in this condition. This phenomenon is not a contradiction of the statement made in the previous article that the liquid is not stable below the melting point, for the surfused liquid is unstable. If the water at -12°C is agitated by a stirrer of some sort, or if a tiny crystal of ice is introduced, it immediately commences to solidify and its temperature rises to 0°C and remains there until the whole mass is changed to ice. The spontaneous formation of ice at -3°C or -4°C noticed in the first case may be caused by some agitation, perhaps due to the entry of dust from the air. A drop of water has been surfused to as low as -20°C by surrounding it with a liquid of the same density and lower freezing point, and surfusion has also been obtained in the case of phosphorus, sulphur, and naphthalene.

51. The Determination of Melting Points.—If a reasonable amount of the solid is available, it is melted in a test-tube and a cooling curve is obtained, from which the melting point can be read off as explained above.

If only a small quantity of the solid is available, some of it is placed in a short length of capillary tubing which

is attached to the bulb of a thermometer. It is then heated up by immersing the bulb in a suitable liquid and the temperatures at which it melts and solidifies on cooling again are observed. If these differ by less than a degree, the mean is taken as the melting point of the solid, otherwise the experiment is repeated with a slower rise and fall of temperature until the two observed temperatures are within a degree.

The effect of a dissolved substance on the freezing point of a liquid is of great importance in the theory of solutions, and Beckmann devised a method of measuring the freezing point of solutions with the greatest accuracy. It depends on the fact, mentioned in the previous article, that the temperature of a surfused liquid rises to the freezing point and remains constant for some time as soon as solidification commences. Beckmann's apparatus consists of a test-tube closed by a cork, through which a sensitive thermometer T and a platinum stirrer S_1 are inserted (Fig 43). The solution or liquid is poured into the test-tube through the inlet L , which is then stopped by a cork, and is cooled by a suitable mixture M , which is separated from the solution by the air-jacket enclosed in the tube B . The freezing mixture is stirred by the stirrer S_2 and the temperature is allowed to fall a few degrees below the approximate freezing point of the solution, which has already been found. The solution is then agitated by the platinum stirrer until solidification sets in, when the thermometer is observed. The temperature rises and remains constant for some time, this constant temperature is taken as the freezing point of the solution. The determination should

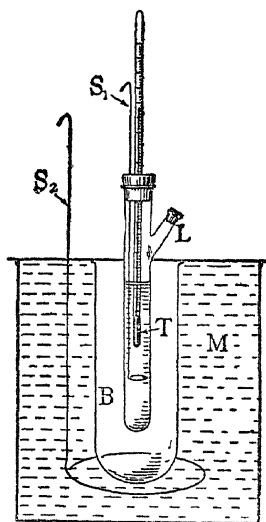


FIG 43 — Beckmann's freezing point apparatus

be repeated several times, the mean of the individual values being taken as the freezing point of the solution

The following results were obtained

(a) The freezing point of a solution is always lower than that of the pure solvent

(b) The depression of the freezing point is proportional to the concentration of the solution, provided it is not too strong

(c) The molecular depression of the freezing point is the product of the molecular weight of the solute and the depression in a solution containing 1 grm of the solute per 100 grm of the solution, and is the same for all solutions which do not conduct electricity

(d) The molecular depression of the freezing point of conducting solutions is abnormally high and tends at large dilution to values which are simple multiples of that for non-conductors

The abnormal depression in the case of electrolytes is connected with the abnormal rise of their boiling point and their osmotic pressure and has been used by Arrhenius as evidence in favour of the dissociation theory of electrolytic conduction

52. The Behaviour of Alloys.—If two metals are mixed to form an alloy, it is found that the melting point is always less than that of either constituent. The melting point also varies in a regular way with the composition of the alloy, as may be illustrated by considering one or two simple cases. Let us suppose that an alloy containing 10 per cent of copper and 90 per cent of silver is melted and then cooled. It is found that it commences to solidify at 880°C , crystals of pure silver separating out, thus making the "mother liquor" richer in copper. At the same time the freezing point of the "mother liquor" decreases and the temperature continues to fall, crystals of silver separating out the whole time. If the same procedure is repeated with an alloy containing 30 per cent of copper and 70 per cent of silver, solidification starts at 770°C , crystals of pure silver again separating out. This continues until the temperature has fallen to 740°C , when the whole alloy freezes as one mass. The solid which crystallises out at this temperature is called a **eutectic alloy** and

contains 40 per cent. of copper and 60 per cent. of silver, and the freezing point is referred to as the **eutectic point**.

If an alloy containing 60 per cent. of copper and 40 per cent. of silver is treated in the same way, it solidifies at 830°C , crystals of pure copper separating out this time and making the "mother liquor" richer in silver. This continues until the composition of the liquid has reached that of the eutectic alloy, when the whole mass freezes as one at 740°C . A graph of the melting point of the alloy and its composition is given in Fig 44, and shows that the eutectic point is the lowest temperature at which the alloy can melt. The fact that the addition of one metal to another causes a lower-

ing of the melting point resembles the effect of a solute on the freezing point of the pure solvent, and suggests that the liquid alloy may be regarded as a solution of one metal in the other. The above example

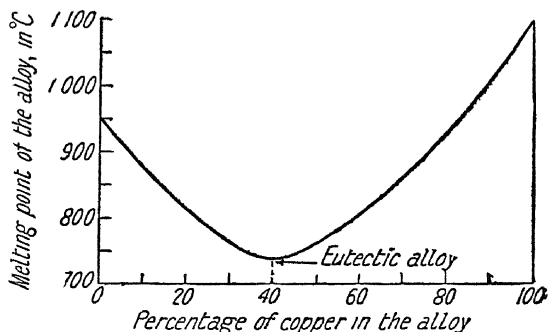


FIG. 44 —The melting points of silver-copper alloys

is typical of many alloys, but more complicated cases occur in which there is more than one eutectic point

53. Freezing Mixtures.—The principles underlying the production of low temperatures by freezing mixtures of ice and salt or ice and calcium chloride are so similar to those governing the behaviour of alloys that it is convenient to treat of them here. When salt is added to pure water, it lowers the freezing point to an extent proportional to the concentration of the solution, the freezing point of a saturated solution being -22°C . When a salt solution is cooled, *pure ice* separates out at the freezing point, just as one of the pure metals crystallises out in the case of the alloy described above. The remaining salt solution

becomes more concentrated and so has a still lower freezing point, and therefore the temperature has to fall to it before more ice can separate out. This fall in temperature and increase in concentration of the solution continue until the temperature reaches -22°C , when the solution will be saturated. *The whole mass now solidifies as one*, that is, a mixture of ice and salt crystallises out. It is like the eutectic alloy, and this temperature corresponds to the eutectic point.

We are now in a position to understand how a mixture of ice and salt produces a temperature of -22°C . When the salt, which will be above 0°C , and ice are mixed, some of the ice will be melted in cooling the salt down to its temperature, and so a saturated solution of salt at 0°C is produced. But ice cannot remain in equilibrium with a saturated solution of salt at 0°C , any more than it can remain in equilibrium with pure water at 20°C . So the ice melts and draws the necessary latent heat from the salt solution and so cools it down. Incidentally this explains why the throwing of salt on to ice frozen on pavements in frosty weather causes it to melt and so removes the danger of slipperiness. This cooling of the salt solution, which is kept saturated by the presence of excess salt, will continue to -22°C , at which temperature the ice is in equilibrium with the saturated solution. This is therefore the lowest temperature which can be reached with this freezing mixture. The cooling process is also aided by the fact that heat is absorbed when salt dissolves in water.

A suitable mixture of ice and calcium chloride will yield a temperature of -55°C , the cooling being specially rapid in this case because of the large negative heat of solution of calcium chloride.

54 The Effect of Pressure on Melting Point.—We shall now consider the influence, if any, of pressure on the melting point of solids, a factor which we have hitherto tacitly ignored. The problem was first solved theoretically by Professor James Thomson using a method based on the two laws of thermodynamics, and his prediction was verified both qualitatively and quantitatively by his brother, Lord Kelvin. Professor Thomson's treatment,

though ingenious, is somewhat involved, and we shall give an alternative solution based on **Le Chatelier's principle**, which states that "if one of the factors of any system in equilibrium is changed, thus disturbing the equilibrium, the effect produced tends to restore that factor to its original value." This principle is based on the two laws of thermodynamics and is of great importance in physical chemistry. It has also many applications in physics, of which Lenz's law in electro-magnetic induction is perhaps the best known. We shall give one simple example of its application in order that its use in the present problem may be thoroughly appreciated. If a gas is heated, it expands. This is just what Le Chatelier's principle predicts. The system is a gas contained in a cylinder, say, with a piston on which the external force just balances that due to the pressure of the gas at the given temperature. When the temperature is raised, the force due to the pressure of the gas must change and so the equilibrium is disturbed. The effect which occurs will try to restore the factor which has changed to its original value. This factor is the temperature of the gas. So the effect will try to cool the gas, and the only way to do this is for the gas to expand.

We will suppose that a mixture of ice and water at 0°C is contained in a cylinder closed by a piston and subjected to a pressure of one atmosphere. The ice and water are in equilibrium at this pressure. Let the pressure be increased to several atmospheres by pushing in the piston. If the equilibrium is disturbed, by Le Chatelier's principle an effect will be produced which will try to restore the pressure to its original value, one atmosphere. This can only be done by the mixture contracting, so some ice will melt, since a decrease in volume accompanies this change. The necessary latent heat will be obtained at the expense of the rest of the mixture of ice and water, which will be cooled, and this drop in temperature will continue until the ice and water are in equilibrium at the new pressure. So we have proved that, in the case of ice and of all substances which contract on melting, an increase of pressure lowers the melting point. It is easy to see that the opposite is the case for substances which expand on melting. The

quantitative relation between the increase in pressure and the change in the melting point is derived in Art 141 as a consequence of the two laws of thermodynamics. It is sufficient to say here that the decrease in melting point in the case of ice works out to be 0.0075°C per atmosphere.

The most accurate experiments to test this prediction were performed in 1880 by Dewar, who measured the melting point of ice at various pressures up to 700 atmospheres. His work is especially valuable, because the theoretical value for the lowering of the melting point is known most accurately in the case of ice. His apparatus consisted of an iron bottle B, immersed in melting ice, to which a

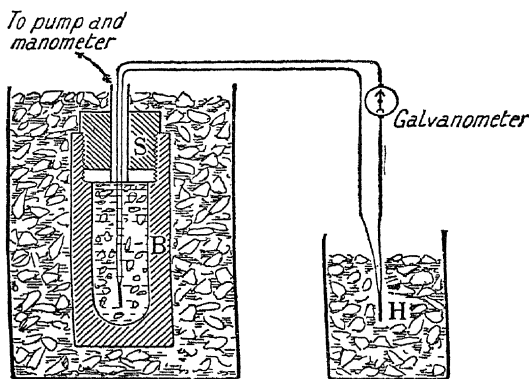


FIG. 45

pump and manometer were attached (Fig 45). The bottle was filled with a mixture of ice and distilled water, carefully freed from air, and was closed by the screw S. The temperature of the ice and water was read by a thermo-couple, one of whose junctions, H, was kept at a fixed temperature by immersing it in melting ice. The pressure was increased by steps of 25 atmospheres, and the temperature of the ice and water was read when it was steady, showing that they were in equilibrium once more. Dewar found that the melting point of ice is lowered by increase of pressure, and that the decrease in melting-point is proportional to the increase in pressure up to 700 atmospheres and is

equal to 0.0072° C. per atmosphere This result forms a striking confirmation of the theoretical prediction outlined above

55. Regelation.—It was discovered by Faraday that, if two pieces of ice are pressed together, they form one solid piece after the pressure is released. This phenomenon is called **regelation**, and is explained by the lowering of the melting point of ice by pressure The parts of the ice in contact are under pressure and will therefore melt if the temperature of the ice is not below 0° C As soon as the pressure is released, the film of water formed at once solidifies again and cements the two pieces together. This has actually been done with the ice under warm water

Another well-known experiment illustrating regelation consists in cutting through a block of ice with a metal wire without breaking it into two pieces The block of ice is placed on two suitable stands and the wire with a weight hanging on each end is slung over it. The wire slowly sinks through the ice, which, however, remains one solid piece, and will break no more easily at the place where the wire has gone through than anywhere else. The explanation of the phenomenon is as follows The weights hanging on the wire cause it to exert a considerable pressure on the ice, and the melting point is thereby lowered to such an extent as to cause it to melt The wire sinks into the ice and the water is squeezed out above it, and being relieved of the pressure of the wire at once solidifies again. This accounts for the block not being split into two pieces; the damage automatically repairs itself as soon as the wire passes on This process continues until the wire has gone right through the ice. It should be noticed that above the wire solidification and so evolution of latent heat is occurring, the converse taking place below it So the latent heat required to melt the ice below the wire comes from that evolved by the water solidifying above it. Therefore copper will cut through the ice more quickly than iron, because it is the better conductor, and string is too bad a conductor to cut through at all.

Regelation explains why snowballs can be made with ice when it is fairly cold but not when it is very cold When the small crystals of snow are pressed together, the

melting point may be lowered below the temperature of the snow if it is only a degree or so below 0°C . The snow therefore melts and the water so formed freezes as soon as the pressure is released and binds the particles of snow into a compact mass. But if the snow is several degrees below 0°C , it will be impossible to apply sufficient pressure to lower the melting point of ice below the temperature of the snow. So the snow will not bind into a snowball, but remains powdery.

The possibility of skating is also due to regelation. At first only a very small area of the blade is in contact with the ice and so the large pressure set up will be quite sufficient to melt the ice however cold. The water so formed acts as a lubricant and enables the skate to slide smoothly over the ice. Incidentally it freezes again as soon as the skate passes on. The melting of the ice due to the very high initial pressure of the blade causes it to sink in until the pressure has been reduced to such a value by the increased area of contact, that the melting point of the ice is equal to its actual temperature. After that the blade does not sink in any further, but it usually sinks in far enough to enable the blade to "grip" the ice. It will not be able to do so if the ice is very cold, and this is why skates will not "bite" in very cold weather. An idea of the magnitude of the lowering of the melting point which may occur can be obtained by considering the case of a man weighing 150 lb skating on the outside edge, whose area may be taken as 0.01 sq in. The pressure exerted on the ice is 15,000 lb per sq in. or 1000 atmospheres, and the lowering of the melting point is 7°C .

56. Change of State: Liquid to Vapour.—If a flask of water is heated by a bunsen, its temperature increases rapidly at first, and after a time a stream of bubbles is seen to rise to the top of the water and escape from the surface. These are due to the expulsion of the dissolved gas by the rise in temperature. Then smaller bubbles will make their appearance, but they collapse before reaching the surface of the water. When the temperature reaches 100°C or thereabouts, these bubbles will grow larger and rise right to the top of the water and burst. They are bubbles of steam, and this process is called **boiling** or **ebullition**.

It may be defined as the conversion of a liquid into a vapour accompanied by the formation of visible bubbles of the vapour in the liquid. Two thermometers placed in the boiling water and steam respectively show that the conversion involves *no change in temperature* if the water is pure. It is also obvious from the fact that it takes about eight times as long to boil the water away as to bring it to the boil, that the change requires a considerable amount of heat. Such heat is called latent heat, and the precise definition of the term and its experimental determination have been dealt with in Art. 16. Lastly, a casual observation of the boiling is sufficient to show that a large increase in volume occurs when water is changed into steam; as a matter of fact 1 cubic inch of water forms about 1 cubic foot of steam.

A careful observer will have noticed "steam" rising from the surface of the water before it actually begins to boil. What he sees is not really steam at all, but tiny drops of hot water forming a cloud. This shows that the water has been changing to steam at the surface, the process becoming more rapid as the temperature rises, and the steam so formed rises and condenses on meeting the colder air. This invisible change from the liquid to the gaseous state occurring at the surface of the liquid is called **evaporation**. Familiar examples are the slow and invisible disappearance of a puddle of water on a dry or windy day, or the drying of the dew off the grass under the influence of the sun on a hot summer morning. Evaporation resembles boiling in that it involves no change in temperature, and is accompanied by an absorption of heat and a change of volume. But it differs from it in that it can take place at any temperature, while boiling occurs at a definite temperature under a given pressure.

57. Evaporation.—We now proceed to a survey of the experimental facts concerning evaporation and one or two applications, deferring the explanation of the facts to Chapter IX on the kinetic theory of matter. The apparatus shown in Fig. 46 is set up and the tubes are filled with mercury. The movable tube R is raised until the mercury in the other one flows through the tap T, which is then closed. If the movable tube is now lowered sufficiently, the mercury

on the other side will also begin to fall, leaving a Torricellian vacuum above it. The difference in levels, P_0 , is measured, and is equal to the atmospheric pressure. A few c.c. of the liquid under investigation, say water, are poured into the space above the tap, which is opened to allow a drop or two to fall into the space above the mercury. It immediately evaporates, and the difference in levels of the mercury is a little less than before, showing that the vapour is exerting a pressure. If the volume of the vapour is changed by lowering or raising the movable tube, the

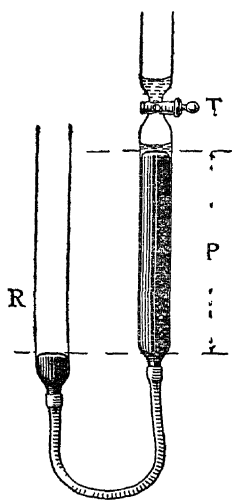


FIG 46

difference in levels also changes showing that the pressure of the vapour depends on its volume. A systematic investigation shows that the vapour obeys Boyle's law to about 2 per cent, the deviation getting more marked as the pressure increases. If a few more drops of the liquid are added, they also evaporate and increase the pressure of the vapour. A stage is reached, however, when further addition of the liquid causes no more evaporation and no further increase in pressure, and a visible amount of the liquid collects above the surface of the mercury. The vapour is now said to be **saturated** in contra-distinction to its former condition, when it was **unsaturated**.

If the volume of the saturated vapour is increased or decreased it causes no change in the difference in levels, P , of the mercury but merely further evaporation or condensation respectively. Therefore the pressure of the saturated vapour, or its vapour pressure as it is called, is independent of the volume and depends only on the temperature. The numerical value of the vapour pressure is equal to $P_0 - P$, and it is found to be the maximum pressure which the vapour can exert at the given temperature. By surrounding the space containing the vapour with a water-jacket, the vapour pressure can be measured at various temperatures and is

found to increase with rise of temperature, the rate of increase becoming more rapid at higher temperatures. Finally, the substitution of other liquids for water shows that the vapour pressure of different liquids at the same temperature is widely different.

The term **vapour** has been frequently used in the foregoing description, and it is convenient to specify at this stage the precise difference in meaning between it and a gas. Experiments are described later on in this book (Chapter X), which show that there is a temperature for every gas above which it cannot exist in the liquid state. However great a pressure is applied, it is impossible to liquefy the gas if it is above this temperature, called the **critical temperature**. The term vapour will be restricted to a gas below its critical temperature, that is, under such conditions that it can be liquefied. The word **gas** will be used indiscriminately to denote a substance either above or below its critical temperature.

If the above experiments are repeated without bothering to drive out the air above the mercury in the closed tube, precisely the same results are obtained as before. The pressure of a given mass of unsaturated vapour occupying a given volume at a given temperature is the same in the presence of air as in its absence. This is in accordance with **Dalton's law of partial pressures**, which states that the pressure exerted by each constituent of a mixture of gases is the same as that which would be exerted by each gas if it alone occupied the total volume now filled by all the gases. The total pressure of the mixture is equal to the sum of these partial pressures, as they are called. If sufficient liquid is present above the mercury to saturate the enclosed space, the vapour pressure is the same as before, the only effect of the air in this case is to cause a longer time to elapse before saturation is actually attained. It should be added that at high pressures the vapour pressure is a little less than that in a vacuum.

We are now in a position to consider the conditions governing evaporation in an open space. A puddle in the road will evaporate if the air above it is unsaturated with water vapour, if not, the puddle will not evaporate. Hence we see why wet roads dry up so slowly on a calm "damp"

day ; the air above the road is saturated or nearly so (that is why the day feels " damp ") , consequently there is nothing to make the water start evaporating, and as there is no wind, no fresh supply of unsaturated air is presented to the water. But a dry windy day dries up the roads quickly, because the unsaturated air promotes evaporation, and as soon as the water has started to saturate one lot of air, a fresh supply of unsaturated air is presented to it by the wind. An interesting example of these principles is the explanation of a " muggy " day or a moist humid heat. The temperature is not necessarily high on such a day. But it will be found that the air is nearly or perhaps completely saturated with water vapour for that temperature. Consequently the evaporation of perspiration, which is Nature's way of keeping the body temperature uniform, is retarded or even stopped and gives rise to an oppressive feeling, because the body finds difficulty in disposing of its surplus heat.

We shall now sum up the facts we have established in connection with evaporation. An unsaturated vapour is one which is exerting less than the maximum pressure for that temperature ; its pressure depends both on the volume and the temperature ; a vapour in the absence of its liquid is likely to be unsaturated.

A saturated vapour is one which is exerting the maximum pressure for that temperature , its pressure depends only on the temperature and is entirely independent of its volume ; a vapour in equilibrium in the presence of its liquid is bound to be saturated.

The vapour pressure of a liquid increases with temperature ; different liquids have widely different vapour pressures at the same temperature.

Evaporation may occur at any temperature , the sole factor governing it is the state of the air in the neighbourhood of the liquid as regards the amount of vapour in it.

58. The Cooling due to Evaporation.—We have seen that if the space in the neighbourhood of a liquid is not saturated with its vapour it will commence to evaporate. If there is no supply of heat, it will draw the necessary latent heat from its surroundings, that is, it will cool itself. If a few drops of ether or methylated spirits are dropped on

the hand, they immediately evaporate and cool the part of the hand they were dropped on. Sufficient cooling can be produced in this way to render the nerves in the neighbourhood insensible, which is what the dentist does when he extracts teeth by "freezing."

A simple experiment to illustrate the cooling due to evaporation consists in standing a beaker of ether on a few drops of water on a wooden block. If bubbles of air are blown through the ether to promote rapid evaporation, sufficient cooling can be produced to freeze the water and enable the block of wood to be picked up by the beaker.

Water can even be frozen by its own evaporation, and one way of doing this is with **Wollaston's cryophorus** (Fig 47). It consists of two bulbs F and C, the former being filled with water and the rest of the apparatus being exhausted before it is sealed off. The bulb C is immersed in a freezing mixture, or better still, in liquid air; this condenses the water vapour in the bulb, and so some of the vapour above the water in F flows in to take its place and is in its turn condensed.

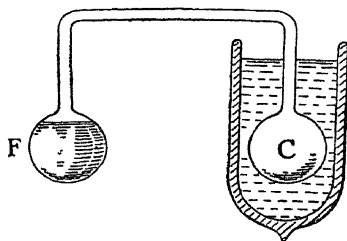


FIG 47

The space above the water is now unsaturated, and so evaporation commences and continues as long as water vapour is being condensed in the bulb C. If the cooling is so rapid that the water cannot obtain the necessary latent heat fast enough from the surrounding air, it will cool itself until it freezes. It may be necessary to surround the bulb F with flannel or some poor conductor before the water will freeze, in order to diminish the rate at which it can draw heat from its surroundings.

It has already been mentioned that the oppressiveness of a "muggy" day is due to the saturation of the air retarding or stopping the evaporation of perspiration and its attendant cooling. A more unpleasant effect is the intense chill experienced after getting wet through. This is due to the fact that the latent heat required by the water

as it evaporates is drawn from the body. It is well known that this cold due to allowing wet clothes or excessive perspiration to dry on one is far more dangerous than that due to a cold wind. This is easily understood in view of the high value of the latent heat of steam.

59. The Electrolux Refrigerator.—We shall now describe the Electrolux refrigerator, which is an admirable practical application of the cooling due to evaporation and

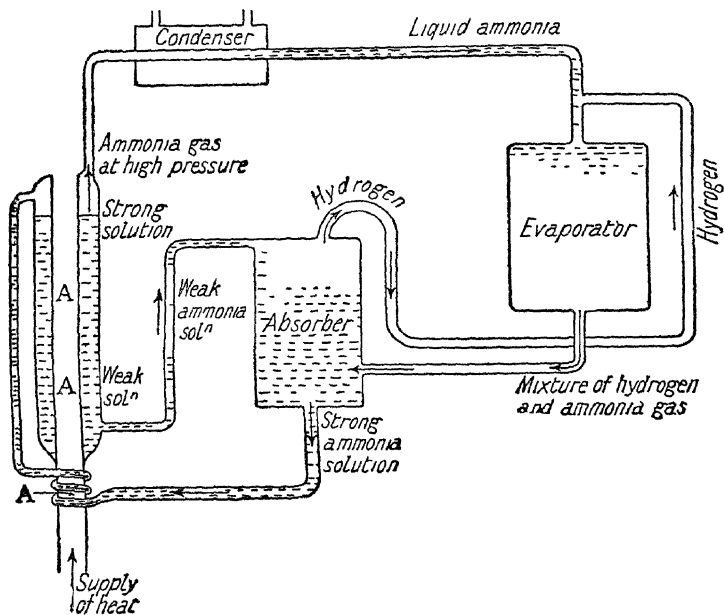


FIG 48

Dalton's law of partial pressures. A refrigerator is a machine for the artificial production of cold, and is designed either to maintain a chamber for the storage of perishable food at a low temperature or to keep a brine-bath well below 0°C for the manufacture of ice. In addition to the Electrolux, there is also a vapour compressing type, which is described in Art 134. A diagrammatic sketch of the Electrolux refrigerator is shown in Fig 48, and it will be

seen that the substances used are liquid ammonia, the refrigerant, an inert gas, hydrogen, and a solution of ammonia in water. The evaporator is immersed in the brine-bath or the chamber to be cooled, and the liquid ammonia is caused to evaporate here in a way which will be explained below. It extracts the necessary latent heat from the surrounding vessel and thereby cools it. The ammonia gas is then led to the condenser by a rather complicated process which will be dealt with shortly, and is there condensed by a stream of cold water. This carries away the latent heat which was absorbed from the vessel to be cooled, and the liquid ammonia returns to the evaporator to extract a further quantity of heat.

We shall now consider how the liquid ammonia is made to evaporate and to pass from the evaporator to the condenser. When the liquid ammonia reaches the evaporator, it encounters a stream of hydrogen. Since all parts of the circulating system are in communication with one another and there is only a slow flow of gas and liquid round it, the total pressure at all parts of the system must be the same. Hence the sum of the partial pressures of the hydrogen and ammonia vapour in the evaporator is equal to that of the ammonia vapour in the condenser. If there is sufficient hydrogen present, it is evident that the partial pressure of the ammonia gas in the evaporator will be less than the saturation pressure even at the low temperature of the evaporator, and so evaporation will be promoted with its attendant cooling.

The mixture of hydrogen and ammonia gas being heavier than the hydrogen sinks to the bottom of the evaporator and flows to the absorber, where it meets a weak solution of ammonia in water. The ammonia gas at once dissolves in this solution as it has great affinity for water and the hydrogen rises to the top and returns to the evaporator. The ammonia solution, which increases in strength as it sinks to the bottom of the absorber, is kept circulating by heat applied at AAA in much the same way that the circulation is maintained in a central heating system. At the same time some of the ammonia is driven off from the water in the boiler, thus once more decreasing the strength of the solution, which afterwards returns to the absorber.

The ammonia gas is now freed from water vapour by passing it through a subsidiary condenser (not shown in the diagram), after which it passes on to the main condenser where it is liquefied, the latent heat emitted being carried away by the stream of cold water running through the condenser. The liquid ammonia now returns to the evaporator and the cycle of operations is repeated as long as the cooling water is kept running through the condenser and the supply of heat at AAA is maintained.

We see that Dalton's law of partial pressures is made use of in making the liquid ammonia evaporate and it is the cooling due to this evaporation which produces and maintains the low temperature required. We may also point out that this instrument is yet another example of the contention that, sooner or later, new physical principles find a practical application. In this case some hundred years has elapsed between the discovery of Dalton's law and its application to the Electrolux refrigerator, but it is no less successful for all that. It is the knowledge of Dalton's law that enabled the method of promoting the evaporation of the liquid ammonia by the use of an inert gas to be thought out. The lag between the discovery of a new physical principle and its commercial application is growing less year by year, and it is essential that it should continue to do so, since upon this depends the material, and hence the cultural and spiritual development of humanity. For commercial prosperity brings leisure, and without leisure there can be no culture and no opportunity for the development of the spiritual side of man's nature.

60. Ebullition.—We have seen that the two characteristic features of boiling are the appearance of bubbles of the vapour in the body of the liquid and the fact that it will only occur at a definite temperature. We are now in a position to explain the relation between these two features in terms of what we have learned of evaporation.

When a liquid begins to boil the bubbles of vapour rise from isolated points on the side of the containing vessel and not from points in the body of the liquid. They are formed by the evaporation of water into a small bubble of air clinging to the side of the vessel, and the occluded gas which is present in the walls of any vessel maintains the

supply as each bubble floats to the top of the liquid. When the temperature of the liquid is below its boiling point, the bubble cannot grow since the sum of the pressures of the vapour and the gas of the bubble is less than the hydrostatic pressure due to the atmosphere and the liquid. As the temperature rises, a point will be reached due to the rapid increase of vapour pressure with temperature when the total pressure inside the bubble is equal to or just exceeds the external pressure. The bubble will now begin to grow, and further evaporation will occur until it is light enough to detach itself from the side of the vessel and rise to the surface of the liquid. *So we see that boiling can only occur at the temperature at which the vapour pressure of the liquid is equal to the external pressure.* This is why it occurs at a definite temperature for a given pressure.

The truth of this explanation can be verified with the apparatus shown in Fig. 46. For the sake of simplicity water will be chosen as the substance for the test. It is merely necessary to surround the closed tube by a steam jacket and measure the vapour pressure of water at this temperature. It is found that the levels of the mercury in the two tubes are the same, showing that the vapour pressure of water is equal to atmospheric pressure at the temperature of its boiling point, thus proving the truth of our explanation.

61. The Variation of Boiling Point with Pressure.—

We can now carry the argument a stage further. If the external pressure on the liquid is altered, it follows that it will boil at a different temperature, the temperature at which the vapour pressure is equal to the new external pressure. Therefore an increase in pressure should raise the boiling point of a liquid and a decrease should lower it.

This prediction, which is quite a good example of the way in which the ideal scientific theory should lead to a search for new facts, can easily be verified experimentally. First of all it can be done in a qualitative way by boiling some water in a round-bottomed flask until all the enclosed air has been expelled. The flask is then closed and cooled under a stream of cold water; after a time the water begins to boil because the pressure has been greatly reduced by

the condensation of the steam. It is possible to get water to boil at a temperature as low as 40°C by this means. Of course the water does not boil for very long, since the steam evolved soon raises the pressure to a value above the vapour pressure of water at its given temperature. Secondly, a quantitative investigation of the relation between the boiling-point of water, say, and the external pressure can be made with the apparatus shown in Fig 49. The water is heated in the flask F and the temperature of the steam is measured by the thermometer T. It is better to measure the temperature of the steam rather than that of the boiling water, as the latter is affected by the presence

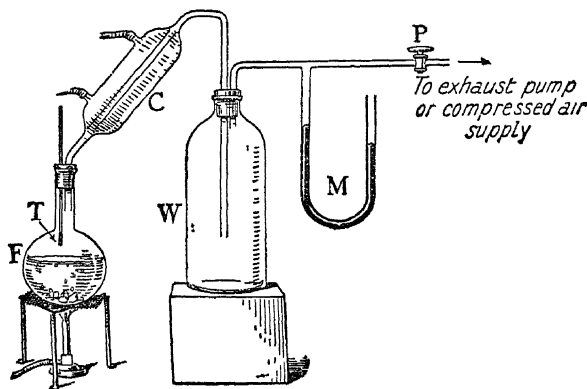


FIG 49

of impurities and the nature of the containing vessel. The steam is condensed by the condenser C as fast as it is formed both to prevent waste of the liquid and to stop the pressure from increasing due to the accumulation of steam. The pressure on the water can be adjusted to any desired value by opening the tap P and turning on either compressed air or an exhaust pump. When the required pressure has been obtained, the tap P is closed and the water is heated until it is boiling steadily. Quiet and regular boiling is promoted by putting a few pieces of broken porcelain in the bottom of the flask. The temperature at which the water boils is read on the thermometer T and

the pressure is obtained from the mercury manometer M. This experiment verifies completely the prediction that increase and decrease of pressure produce rise and fall respectively in the boiling point of a liquid.

A few numerical results will be given to illustrate the order of magnitude of the effects obtained. At a pressure of 46 mm. of mercury water boils at 0°C ; if the pressure is raised to 92 mm. the water still boils as low as 50°C , while at a pressure of 16 atmospheres, approximately that in the boiler of an express locomotive, it boils at 200°C .

Various applications are made of this variation of boiling point with pressure. The height of a mountain can be calculated from a knowledge of the pressure of the atmosphere at its summit. It is often inconvenient to take a barometer to the top, and so the pressure is measured indirectly by finding the boiling point of water at the top of the mountain. Again it may be desired to purify a liquid by distillation; if, however, it undergoes chemical decomposition at a temperature below its boiling point, then the distillation is carried out under reduced pressure so as to prevent this. In order to sterilise surgical instruments it is necessary to heat them to a temperature considerably above 100°C , which is done by placing them in water boiling at high pressure. The same way of obtaining a temperature well above 100°C . for cooking purposes is used in the pressure cooker.

62. Delayed Boiling.—When a flask of water is boiled we have seen that the bubbles of steam start from a few isolated points on the side of the flask and the temperature of the water remains constant. If the boiling is continued for some time, it will be noticed that the bubbles are getting smaller and less frequent and a thermometer will show that the temperature of the water is rising. After a time, the boiling will cease altogether and the temperature may rise as far as 106°C . Then a few large bubbles of steam will be produced explosively and all will be quiet once more for a time. This process will be repeated at intervals, and is known as **delayed boiling** or **bumping**. The second name refers to the bumping noise which is made by the whole body of the liquid falling back to the bottom of the

flask after having been lifted by a large bubble of steam. The cause of delayed boiling is revealed by the fact that it can be suppressed by putting a few pieces of broken porcelain or some sand into the water. The boiling at once becomes regular and quiet and the temperature resumes its normal value. This suggests that the porcelain or sand supplies bubbles of gas to serve as nuclei into which the water can evaporate. This hypothesis can be tested by boiling water in a vessel which has been specially cleaned to remove any dust, grease, or occluded gas which might serve as a nucleus for evaporation. The water itself must be previously boiled to expel the dissolved air. When the experiment is tried, it is found that it is possible to heat the water up to 137°C before it boils and then it does so with explosive violence. But immediately porcelain or some sand is added, normal boiling sets in. A still more striking confirmation of our hypothesis is furnished by Dufour's experiment. He prepared a mixture of oils of high boiling point, whose density was the same as that of water. He was able to heat a bubble of air-free water enclosed in the oil to 178°C without any boiling taking place.

We may, then, take it as established by experiment that delayed boiling is due to the absence of any nucleus, such as bubbles of gas or particles of dust, to promote evaporation and the subsequent formation of bubbles of vapour. It is a comparatively simple matter to extend our explanation of ebullition to explain this fact. If there is no nucleus around which the molecules of steam can collect in their attempt to form a bubble, the radius of any bubble they may form themselves must be very small. This involves taking account of the pressure due to surface tension. The blowing of soap bubbles shows that the pressure inside them is greater than that outside; this is needed to counteract the force due to the surface tension of the soap solution, that property of the surface of the solution which makes it behave like a stretched skin and therefore always try to shrink. The surface of water also exhibits this same property and therefore a bubble of steam in water will experience a pressure due to surface tension in addition to the hydrostatic pressure. If the bubble is a sphere of

radius r and the surface tension of water is T , the pressure p due to surface tension is given by

$$p = \frac{2T}{r}.$$

For a bubble of radius 1 mm due to steam evaporating into a gas bubble this is equal to $\frac{2 \times 75}{10^{-3}} = 1500$ dynes per sq cm = 11 mm of mercury and is quite negligible. But if sufficient molecules collect together in the absence of gas bubbles to form a bubble of 10^{-4} mm. in radius, the pressure due to surface tension is given by

$$p = \frac{2 \times 75}{10^{-5}} = 15,000,000 \text{ dynes per sq cm} \\ = 15 \text{ atmospheres, approximately,}$$

the surface tension of water being taken as 75 dynes per cm. Now the water must be heated to such a temperature that its vapour pressure is equal to the sum of the pressure of surface tension and the external pressure, that is, 16 atmospheres in this case, if the bubble is to persist. Such a pressure is only reached at 200°C . Therefore we see that water can be heated to this temperature before bubbles of this initial size begin to grow. But when they do grow, they do so with explosive violence, for the equilibrium is unstable. As the bubble grows the vapour pressure remains constant, because the evaporation is able to keep pace with the increase in size of the bubble, provided that the heat is supplied fast enough. But the external pressure due to surface tension decreases with increasing radius, and so the excess of the internal over the external pressure increases rapidly and causes the bubble to burst violently.

63. Determination of Boiling Points.—It is well known that the temperature of a boiling liquid and its vapour are the same, while the temperature of the vapour given off by a boiling solution is the same as that of the pure boiling solvent and not that of the solution. On this account the procedure to be adopted in determining a boiling point depends on whether we are dealing with a pure liquid or a solution. We shall consider first of all the case of a pure liquid.

In determining the boiling point of a liquid, the thermometer is placed in the vapour with its bulb about one inch above the surface of the liquid to avoid splashing. This is done because the temperature of the liquid may get above the normal boiling point owing to delayed boiling, traces of impurity or even the effect of the containing vessel. A hypsometer is used and the experiment is carried out in

the same way as in the determination of the upper fixed point of a thermometer.

If only a small quantity of the liquid is available, a method is employed which makes use of the fact that the vapour pressure of a liquid at its boiling point is equal to the atmospheric pressure. The liquid is introduced into the apparatus for finding vapour pressures shown in Fig 46, so that the space between the mercury and the tap T contains only the liquid and its saturated vapour. The closed tube is now jacketed with a suitable liquid which is heated until the mercury levels in the two tubes are the same. The vapour pressure of the liquid above

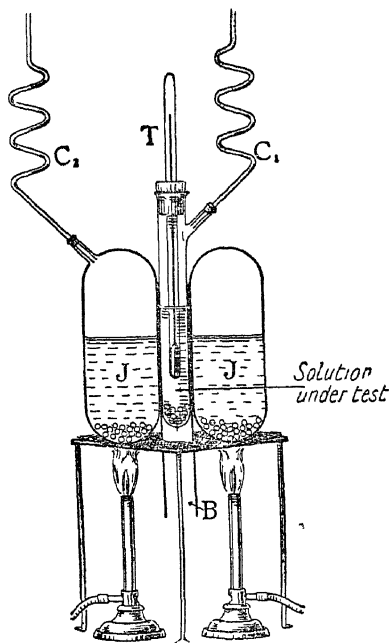


FIG 50

the mercury is now equal to the atmospheric pressure and the temperature of the jacket is read and is equal to the boiling point of the liquid.

We shall now consider the accurate determination of the boiling point of solutions, a subject of considerable importance in physical chemistry. Since the temperature of the vapour is equal to that of the pure solvent and not that of the solution, it is necessary to put the thermometer in the

boiling solution. This makes it imperative to avoid the error due to delayed boiling. It is prevented by putting a few pieces of porcelain into the liquid, and also by heating it by a vapour whose temperature is just higher than the boiling point of the solution. Beckmann's apparatus for the determination of boiling point of solutions is shown diagrammatically in Fig. 50. The liquid whose boiling point is to be found is placed in the inner tube, which is supplied with a Beckmann thermometer *T* and a condenser *C* to prevent the escape of the vapour from the boiling solution. A platinum wire sealed through the bottom of the tube and some porcelain tubes are placed in the liquid to prevent delayed boiling. The liquid is heated by means of a jacket *J* containing a liquid whose vapour is just hotter than the boiling point of the solution. This jacket contains a few porcelain tubes to ensure quiet and regular boiling, and is heated by two burners. The inner tube is carefully screened from the direct effect of the burners by the asbestos tube *B*. This precaution is observed in order to prevent the delayed boiling which would otherwise be certain to occur. The burners are turned on and the liquid is boiled quietly until the solution is observed to be doing the same. The temperature of the solution is read at intervals on the Beckmann thermometer, and the mean of the observations is the boiling point of the solution.

We may summarise here the results which have been obtained concerning the influence of dissolved substances on the boiling point of a liquid.

(a) The boiling point of a solution is higher than that of the solvent. This is due to the fact that the solute causes a decrease in the vapour pressure of the solvent.

(b) The increase in boiling point is proportional to the concentration of the solution.

(c) The molecular elevation of the boiling point is the elevation in a solution containing 1 gram-molecule of the solute in 100 grms. of the solvent, and is constant for all solutions of the same solvent which do not conduct electricity. Its value for aqueous solutions is about 5°C .

(d) The molecular elevation of the boiling point of solutions which are conductors of electricity is abnormally high.

This last fact corresponds with the similar anomaly in the lowering of the freezing point, and in the same way supports Arrhenius' theory of electrolytic dissociation. Further details of this subject can be found in any text-book of physical chemistry.

EXAMPLES ON CHAPTER VI

1 Give an account of surfusion, and show how it has been applied to the determination of the freezing point of solutions.

2 Give a discussion of the production of low temperatures by freezing mixtures.

3 How can the effect of pressure on the melting point of a solid be investigated theoretically? Describe any experiments which have been performed to test the predictions.

4 Discuss the phenomenon of regelation and describe some examples of it in everyday life.

5 Describe fully how you find the change in volume of 1 grm. of ice at 0°C in changing to water at 0°C (a) by a direct method, (b) by an indirect method.

6 Give a critical account of an experiment designed to investigate the simple properties of a vapour, and apply the results obtained to the study of the factors governing the rate of evaporation of a puddle in the road.

7 On coming downstairs in the morning to a room in which the windows and door have been closed overnight, it is found that the windows are "streaming" with water. Describe the conditions which are likely to produce this result and show how they lead to the deposition of the water on the windows.

8 Assuming the facts concerning saturated vapours, discuss the physical principles underlying ebullition, and state how far your predictions are verified by experiment.

9 State the facts of "delayed boiling," and show how they can be explained.

10 Describe and explain the effect of pressure on the boiling point of a liquid (*Tripos*, Part 1).

11 What factors affect the boiling point of a liquid? Show how the observation of the boiling point of a pure liquid may be made the basis of a method of measuring approximately the height of a mountain (*Camb. Schol.*)

12 Early Alpine travellers used to carry with them an apparatus for measuring the boiling point of water in order to ascertain the heights of peaks above sea-level. Nowadays an aneroid barometer is used instead. Explain the principles upon which these methods are based (*Oxford Schol.*)

13 A physics laboratory is in a building 20 metres (70 feet) high. Would it be possible to detect the difference in the boiling point of water at the top and bottom of the building (a) with an ordinary mercury thermometer, (b) with a platinum resistance thermometer? Assume the density of air is constant and equal to 0.00125 gm per cc, and that the change in boiling point at 100° C is 1° C for every 27 mm of mercury change in pressure.

14 What is the boiling point of water at the top of Snowdon, 1000 metres high, on a day when the barometer reads 76.0 cm at sea-level in the neighbourhood? You may assume that the density of the air is constant, and use the same numerical values for the constants you require as in the previous question.

15 Write an account of the Electrolux refrigerator, emphasising the physical principles on which it is based.

CHAPTER VII

THE PROPERTIES OF VAPOURS

64. The Determination of Vapour Pressure.—The measurement of the vapour pressure of liquids and its variation with temperature is a matter of some importance, both theoretically and practically. Its theoretical value lies in the fact that the results can be used as a test of the second law of thermodynamics, while practically they are, in the case of steam, of vital importance to the engineer for the calculation of the efficiency of various types of steam engine. The experimental determinations divide themselves into three main classes according to the range of temperature for which they are designed. One method is adapted for temperatures from 0° C to 50° C, another for low temperatures, and the third for high temperatures. We shall now describe them in this order.

65. Regnault's Method for Temperatures from 0° C. to 50° C.—The fundamental principle of this method is to measure the pressure of the saturated vapour at a known temperature by the depression it produces in a mercury barometer.

Two barometer tubes are set up with their upper ends in a water-bath provided with a plane glass front (Fig 51). The aim of the plane glass front is to avoid errors due to refraction in reading the difference in levels of the barometers. The liquid under investigation is introduced into the right-hand tube with a bent pipette until the space above the mercury is saturated. The water-bath is then heated electrically or cooled according as the determination is to be made at temperatures above or below that of the atmosphere, the water being stirred the whole time to

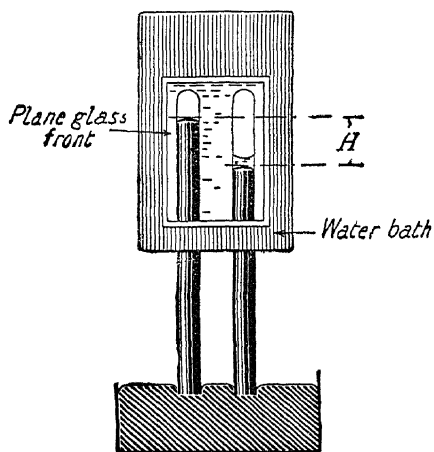


FIG 51

avoid the inequalities of temperature which are otherwise inevitable. When the required temperature is reached, it is read by a thermometer and the difference of levels H of the mercury surfaces in the two tubes is read by a cathetometer (The thermometer, heating coil, and stirrer are not shown in the diagram). Three corrections have to be made to this reading to obtain the vapour pressure of the liquid.

(a) The pressure due to the height h of the liquid above the mercury in the right-hand tube must be allowed for. It is given by $h\rho_e/\rho$, where ρ_e and ρ are the densities of the liquid and mercury respectively at the given temperature, and must be subtracted from the difference in levels H of the mercury.

(b) The effect of surface tension must also be taken into account. It is well known that surface tension causes most liquids to rise up a capillary tube, it also causes mercury to be depressed when placed in such a tube. The amount of the depression or elevation depends, among other things, on the surface tension of the liquid. Now the

surface tension of mercury in contact with water is different from that of a free mercury surface. Consequently the mercury in the left-hand tube will be depressed to a different extent from that in the right-hand side. The difference h_s in the two depressions is found with the apparatus shown in Fig 52. The two tubes are stood in a bowl of mercury, and the air above them is exhausted by means of a pump connected to the side tube C. Dry air is then admitted to the tubes and pumped out, the whole process being repeated several times in order to dry the space above the mercury thoroughly. When this is finally exhausted and the tap T is closed, the two tubes are acting as barometers and the mercury stands at the same level in both. A sufficient quantity of the liquid in question is now introduced into the right-hand tube to saturate the whole space above both tubes and a difference in levels is thereby produced. This is not due to the vapour pressure, which acts equally on both columns of mercury, but to the surface tension effect and to the pressure due to the small column of liquid above the mercury in the right-hand tube. This difference in levels corrected for the pressure of the liquid is the required correction h_s . In the case of water the right-hand side is found to be 0.14 mm. higher than the other, and so this amount must be added to the measured difference in levels H . It is so small that any variation with temperature may be neglected.

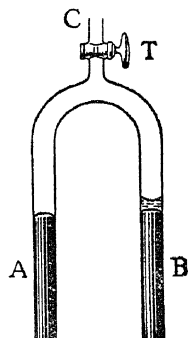


FIG 52.

(c) We now have the vapour pressure p of the liquid at the given temperature t given by the equation

$$p = \left(H - \frac{h\rho_e}{\rho} + h_s \right)$$

cm of mercury at $t^\circ \text{C}$. This should finally be reduced to the corresponding height of mercury at 0°C . in accordance with the principles discussed in Art 36.

66. Vapour Pressures at Low Temperatures.—We shall now describe a method of measuring vapour pressures

which can be used at any temperature lower than that of the atmosphere and is applicable to substances with widely differing vapour pressures. It could be used, for example, to measure the vapour pressure of ice, and has been applied to the case of the permanent gases at temperatures between their freezing and boiling points.

The pressure of the vapour is measured by the manometer M (Fig 53). The space above the mercury on the left-hand side can either be exhausted or opened to the atmosphere, according to the magnitude of the pressure to be measured. The tap T_1 is closed and T_2 is opened, and the

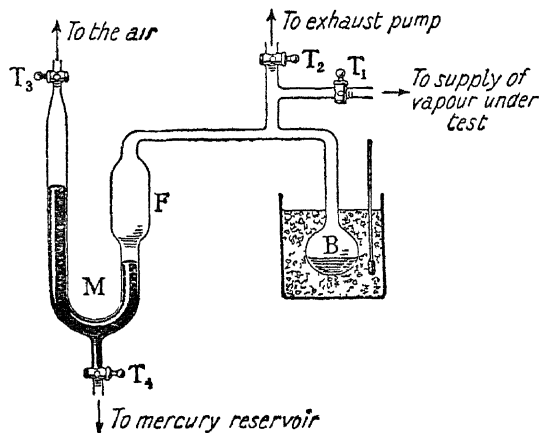


FIG 53

whole apparatus is exhausted. The bulb B is then surrounded by a suitable freezing mixture, and the tap T_2 is closed and T_1 is opened and lets in a supply of vapour, which is at once condensed in the bulb as soon as the apparatus is saturated. When sufficient liquid has been

formed, the tap T_1 is turned off and the difference of levels of the manometer is measured by a cathetometer. The tap T_4 is then opened and mercury is pumped into the manometer until the space F is full. The difference of levels is again measured, and should be the same as before. If the space above the left-hand side of the manometer is exhausted, this difference of levels corrected to 0°C gives the vapour pressure of the liquid at the temperature of the bulb B. If it is open to the atmosphere, it must be added to or subtracted from the height of the barometer according as the left-hand side of the manometer is the higher or

lower The experiment is now repeated at various temperatures throughout the range over which it is desired to investigate the vapour pressure of the given liquid

It is necessary to explain why the vapour pressure measured in this experiment is that corresponding to the temperature of the bulb, although the vapour above the mercury in the right-hand limb of the manometer is at a much higher temperature If this vapour exerted the saturation pressure corresponding to its actual temperature, it would be at a higher pressure than that above the liquid in the bulb, and so vapour would flow from the manometer to the bulb in order to equalise the pressures But any attempt to raise the pressure of the vapour in the bulb merely results in condensation, which continues until the pressure of the vapour throughout the whole apparatus is the same as that above the liquid In fact, equilibrium is established *when the pressure of the vapour is everywhere equal to that at the coldest part of the system*. Therefore the vapour pressure measured in this experiment is that corresponding to the temperature of the bulb, which is obtained from a thermometer immersed in the freezing mixture

67. Regnault's Method for High Temperatures.—As the temperature rises, the vapour pressure increases, and when it becomes greater than about 10 cm the apparatus shown in Fig 51 is no longer suitable The water-bath would have to be enlarged to such an extent that it would be impossible to keep its temperature uniform So Regnault designed an entirely different apparatus for use at high temperatures The method he adopted depends on the fact that a liquid boils at the temperature at which its vapour pressure is equal to the external pressure The mode of operation in the experiment is to find the boiling point of the liquid under a given external pressure, then that pressure is equal to the vapour pressure of the liquid at the temperature of its boiling point In the previous methods, sometimes called statical methods, the temperature is the controlling factor, the independent variable as it were, and the pressure adjusts itself to it But in this experiment, sometimes called the dynamical method because the liquid is continually being boiled away, the rôles are reversed, and it is the temperature which has to adjust itself to a pre-ordained pressure

The liquid under investigation is contained in a copper boiler B, which is connected through a condenser C to an air reservoir R, which leads on to a manometer M and a compressed air or exhaust pump (Fig 54). In performing an experiment the tap P is opened, and the pressure is adjusted to the required value, after which the tap is closed again. The air reservoir R is kept at a constant temperature by immersing it in a water-bath and by increasing the total volume of the apparatus prevents any violent fluctuations in the pressure on the liquid due to the movement of the mercury in the manometer or to the initial production of

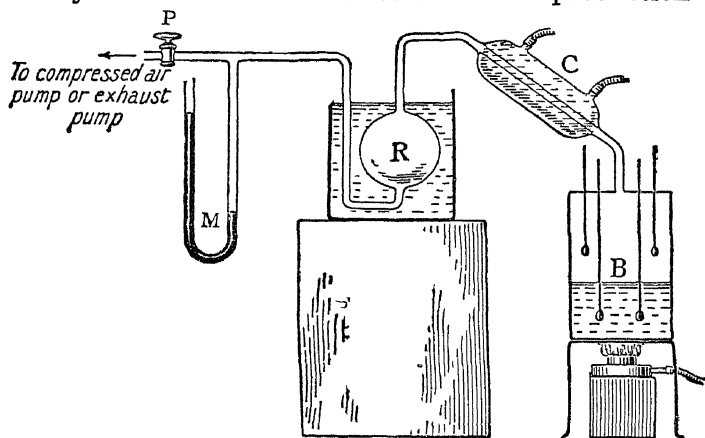


FIG 54

vapour, and enables the pressure to be altered by small amounts. The liquid is now heated, and will commence to boil as soon as its vapour pressure is equal to the external pressure. The vapour produced is condensed in C as fast as it is formed, and so the liquid is not wasted and the pressure is prevented from rising. Delayed boiling is prevented by a few pieces of broken porcelain, and the boiling point is obtained from the mean of the readings of four thermometers, two in the liquid and two in the vapour, all of which are protected from the effect of the pressure in the boiler by enclosing them in iron tubes (not shown in the diagram). The pressure of the vapour corresponding

to this boiling point is read off from the manometer M. The pressure is then altered by a suitable amount and the new boiling point is measured, and so on, until the highest pressure which the apparatus is made to stand has been reached.

Regnault used this apparatus to investigate the vapour pressure of water from 50°C to over 200°C ., where the pressure has reached 28 atmospheres.

It has already been emphasised that, after the experimental facts have been determined, it is essential to classify them in order that their significance may be the better appreciated. As examples of such classification, we have already had Dulong and Petit's law in the case of the specific heats of the solid elements and the ideal gas equation, which expresses to a first approximation the behaviour of all the permanent gases. Many attempts have been made to do the same thing in the case of the variation of vapour pressure with temperature, and several formulæ have been suggested as representing the results, but it cannot be said that they have met with any great success. Their most common failing is that they only agree with the experimental results over a small range of temperature. So we must be content with saying that the vapour pressure of liquids increases with rise of temperature and the rate of increase becomes greater the higher the temperature. It has been possible, however, to compare the results with a theoretical expression derived from the second law of thermodynamics, and an account of this will be given in Chapter XIII.

68. The Determination of Vapour Density.—The fundamental definition of the density of a gas at a given temperature and pressure is the mass of unit volume of the gas measured at that temperature and pressure. There is, however, a rather different definition to which the name vapour density is applied. This is the mass of a given volume of the vapour divided by the mass of an equal volume of air at the same temperature and pressure. The chemist uses hydrogen as the standard substance instead of air.

The measurement of vapour density is the standard way of finding the molecular weight of a substance. By Avogadro's hypothesis equal volumes of all gases at the

same temperature and pressure contain equal numbers of molecules. It follows at once that the vapour density of a substance with hydrogen as the standard is equal to the ratio of the mass of a molecule of the substance to that of a molecule of hydrogen. Since the molecular weight of hydrogen is 2, the vapour density of a substance is half its molecular weight. For this purpose the vapour density need only be found to 5 per cent, for all that is needed is an approximate value of the molecular weight to enable the valency to be fixed. The precise value of the molecular weight is then calculated from the equivalent.

It might appear at first sight, that, apart from the above application, there is very little point in finding the density of gases. Scientific measurements are usually made with a view to testing some hypothesis or other, but the measurement of density can hardly be included under this heading. The work of Dumas, Gay-Lussac, and others was probably undertaken largely as a routine determination of the constants of the various gases. Regnault carried out a series of investigations on the density of water vapour to see if any deviation from Boyle's law occurs as the point of saturation is approached. Nevertheless this field of work was to yield a rich harvest at the hands of the late Lord Rayleigh. Guided by that intuition which is the endowment of genius, he undertook a long series of very accurate measurements of the density of atmospheric nitrogen and chemically prepared nitrogen. After a long series of experiments he found that the density of atmospheric nitrogen was 1.2520 grm per litre, whereas that of nitrogen prepared from ammonia was 1.2507 grm per litre. He interpreted this result as showing that atmospheric nitrogen was not an element but contained other gases which had not yet been discovered, and with Sir William Ramsay he succeeded in demonstrating the correctness of his inference by isolating the rare gases of the atmosphere. It is now less than forty years since this discovery was made, but three of these gases are being utilised commercially in many ways, the neon lamp in television, argon for gas-filled electric lamps and helium for filling airships. This example forms a striking illustration of two principles of wide application, the first is that

fruitful discoveries may be made in the most unpromising places, the second is that the new knowledge discovered by the disinterested worker with no thought of practical application revolutionises commerce. Television would have been impossible without the photo-electric cell and the neon lamp, both are the fruits of the labours of the pure scientific worker

69. The Permanent Gases.—It is usual to find the density of the permanent gases at 0°C and 76 cm pressure. The principle of the method is as follows. A bulb is surrounded with melting ice and filled with the gas whose density is to be found at atmospheric pressure P . It is then closed and weighed. It is now exhausted to a pressure p , closed up and weighed again. Let us suppose that the loss in weight is W grm. If V c c is the volume of the flask at 0°C , the mass of gas in the flask at the end of the experiment occupies a volume V c c at 0°C . and a pressure p and therefore a volume $\frac{pV}{P}$ c c at 0°C and a pressure

P . Therefore W grm is the mass of $\left(V - \frac{pV}{P}\right) = \frac{V(P - p)}{P}$ c c of the gas at 0°C and a pressure P , or $\frac{V(P - p)}{76}$ c c.

at 0°C and 76 cm pressure. The density of the gas is now found from the ratio of the mass to the volume

70. Regnault's Experiments on Water Vapour—It is of interest to see if vapours obey Boyle's law and if so, whether they will continue to do so right up to the point of saturation. We have seen (Art 42) that the permanent gases, which are gases remote from the point of saturation at the ordinary temperatures, obey Boyle's law strictly as far as our experiments go. But we made a reservation that small deviations might be detected by more accurate work. Also it does not seem likely on theoretical grounds that a vapour will obey the law to the very point of saturation, for it is then about to change into the liquid state, in which Boyle's law is quite untrue. Bearing in mind the absence of abrupt changes in nature it seems probable that some deviation from the law will occur before the point of saturation.

We have already described a method of investigating

the relation between the volume and pressure of an unsaturated vapour (Art 57), which led to the result that Boyle's law is obeyed to about 2 per cent. This method cannot by its very nature be specially accurate because the different volumes assumed by the vapour cannot be determined with precision. So Regnault adopted a method of attacking this problem which eliminated this weakness. He decided to see how the density of the vapour depends on its pressure at constant temperature. The vapour was always arranged so as to occupy the same volume which was determined accurately once and for all. If Boyle's law is obeyed, the density of the vapour should be directly proportional to its pressure.

Regnault's experiments were confined to water vapour and were conducted at 100°C under pressures considerably less than atmospheric and at ordinary temperatures under pressures nearly equal to the saturation pressure. A large glass globe was connected both to an ordinary U-tube mercury manometer and to an exhaust pump. A small sealed bulb containing a known mass of water was introduced into the globe, which was exhausted as far as possible, the remaining air being carefully dried. The volume of the air was adjusted to the known standard volume of the apparatus and the pressure was measured by the manometer. The sealed bulb was then broken and the temperature was raised to such a value as to vaporise all the water. The volume of the vapour was adjusted to the known standard volume, and its pressure, together with that of the residual air, was obtained from the manometer, the pressure of the vapour is found by subtracting the pressure of the residual air corrected for temperature from this measured pressure. The mass, volume, pressure, and temperature of the unsaturated vapour having been measured, its density at a known temperature and pressure can be calculated. By introducing different masses of water different pressures can be obtained, and the experiments can be carried out at various temperatures by varying the temperature of the water-bath surrounding the globe.

Regnault found that an unsaturated vapour obeys Boyle's law to an accuracy of 1 per cent, but that the deviations become bigger as saturation is approached. At pressures

exceeding 0.8 of the saturation pressure, the law is no longer true

71. Fairbairn and Tate's Experiments on the Density of Saturated Vapours.—Regnault's experiments on water vapour were carried right to the point of saturation, but the results at the point of saturation were unreliable. It is important to devise an accurate method of measuring the density of a saturated vapour in order to find the extent of the deviation from Boyle's law, which will be greatest here

The experimental determination of the density of a saturated vapour presents serious difficulties. It is easy enough to measure the volume of the saturated vapour, but if saturation is ensured by the presence of liquid, how can the mass of the vapour only be determined? If it is sought to overcome this difficulty by having no liquid present, how can we be sure that the vapour is really saturated? It is evident that we need a method of indicating the precise point at which a vapour ceases to be saturated. Such a method was devised by Fairbairn and Tate. Their apparatus,

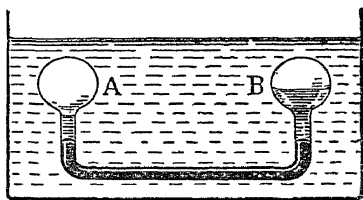


FIG 55

the principle of which is illustrated in Fig 55, consists of two bulbs, A and B, containing different masses of the liquid under investigation separated by a column of mercury. The space above the liquid in each bulb is exhausted and contains only saturated vapour, the whole apparatus is surrounded by a water-bath. If B contains the larger amount of liquid, at ordinary temperatures when there is some liquid present in A, the pressure of the vapour in each bulb will be the same, and so there will only be a small difference in levels of the mercury due to the unequal amounts of liquid in the two bulbs. The water-bath is now heated, but the difference of levels of the mercury remains the same so long as there is any liquid left in A. When the temperature is reached at which all the liquid in A has evaporated and the vapour begins to become

unsaturated, *the difference in levels immediately increases*, because the pressure of the saturated vapour increases more rapidly than that of the superheated vapour. This can easily be seen by a glance at Andrews' isothermals for carbon dioxide (Fig 68). In the same way the difference of levels will cease to alter at that temperature at which the vapour in A becomes saturated when the water-bath is being cooled down again. The procedure in the experiment, then, is to find the temperature at which the difference in levels of the mercury begins to change. The volume of the saturated vapour in A can be measured from the level of the mercury on the left-hand side, and knowing the mass of liquid which was originally put into A, the density of the saturated vapour at the above measured temperature and corresponding pressure can be calculated. Any reader interested in the details of the way in which the experiment was actually carried out should consult Preston's *Heat*, where they are fully described.

Fairbairn and Tate found that the density of saturated steam is invariably greater than that calculated from Boyle's law. For example, they found that the volume of 1 gram of saturated steam at 100°C and 76 cm pressure is 1641 c.c., whereas the value obtained from Regnault's results on unsaturated steam assuming Boyle's law to be true is 1696 c.c. Their results have been corroborated for other vapours by other workers, and so we may say that vapours do not obey Boyle's law up to the point of saturation; they become more compressible than the law would indicate as the point of condensation is approached.

This result suggests a more accurate experimental investigation of the gas laws with a view to seeing if the permanent gases do deviate from Boyle's law. If they do, it would suggest that there is no difference in kind between them and vapours, and that they are only "permanent" because we have not yet succeeded in reaching low enough temperatures to liquefy them. This matter will be dealt with in Chapter X.

Before leaving this subject, it should be mentioned that, while Fairbairn and Tate's general conclusion that gases are more compressible near the point of condensation than is indicated by Boyle's law is still accepted, their values of

the volume of 1 grm of saturated steam are not to be regarded as final. In later experiments Knoblauch, Linde, and Klebe have obtained the value 1677 c c for this quantity, and the lower value obtained by Fairbairn and Tate is probably due to the occlusion of steam by the walls of the containing vessel. This quantity can also be calculated from an equation based on the Second Law of Thermodynamics, and the value so obtained is 1673 c c (Art 141).

72. Victor Meyer's Method.—This method is designed to give a rapid and simple determination of the vapour density of a substance to 5 per cent. with a view to estimating its molecular weight. The apparatus consists of a bulb L with a long stem, which can be closed by the stopper S (Fig 56). A side tube leads from the stem to a pneumatic trough provided with a graduated gas jar for collecting the air displaced by the vapour. The bulb and a considerable part of the stem are enclosed by a jacket H, which can be filled with water or any other suitable liquid whose boiling point is well above that of the liquid to be investigated. The experiment is commenced by removing the stopper S and boiling the water in the jacket, bumping being prevented by a few pieces of broken porcelain. When the temperature of the bulb has attained that of the surrounding jacket, a stoppered bottle B containing a known mass of the liquid under investigation is dropped into the bulb and falls on to some asbestos or glass wool to prevent it from being broken. The stopper S is immediately replaced and the liquid quickly vaporises and forces off

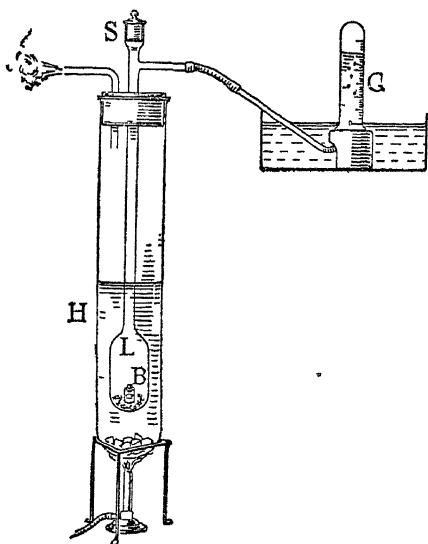


FIG 56.

the stopper of the bottle B. The vapour rises and displaces a mass of air which occupies the same volume as itself at the same temperature and pressure. This air passes into the graduated gas jar G, where its volume is measured at a known temperature and pressure (the temperature of the water in the pneumatic trough and the pressure of the atmosphere corrected for the vapour pressure of water and any difference of levels inside and outside the gas jar). Consequently the volume of the air at N.T.P. and therefore its mass can be calculated. The vapour density is obtained by dividing the mass of the liquid by that of the air. This can be reduced to the vapour density relative to hydrogen knowing the density of hydrogen and air, which can be found by the method outlined in Art. 69. This method is suitable only for substances which are liquid at ordinary temperatures and have a comparatively low boiling point.

73. Relative Humidity.—It has been shown experimentally that there is a maximum pressure for the water vapour in space for every temperature, and that that pressure is independent of whether the space contains air or not. The word pressure here and in what follows refers, of course, to the partial pressure of the water vapour. When the air contains water vapour at this pressure it is said to be saturated. Any increase in the amount of water vapour present or a decrease in temperature merely produces condensation. This is the cause of the formation of clouds, due to the supersaturation of the upper air, of fog when the still air in the neighbourhood of the ground becomes supersaturated, and of the condensation of water on the outside of cold-water jugs or glasses on a dining table due to the local cooling of the air around them. When the air is in this condition it feels "muggy"; this is due to the fact that the perspiration which is continually being formed on our bodies is unable to evaporate, as the air in its vicinity is already saturated, and so one of Nature's ways of keeping the body temperature constant has been thrown out of action. It is the presence of saturated air rather than the high temperature which makes the tropics so oppressive for the white races. Every one is familiar, on the contrary, with a hot dry day, the sun is shining brightly and the

temperature is very high, but the day is not oppressive, because the pressure of the water vapour in the atmosphere is not nearly sufficient to saturate it, and so free evaporation of perspiration with its attendant cooling effect can readily take place. It should be noticed that it is not the absolute pressure of the water vapour present in the atmosphere which determines its "mugginess" or humidity, to use the technical term, but its relation to the saturation vapour pressure at the actual temperature of the air at that time. A given vapour pressure may be sufficient to saturate the air in winter and so produce the impression of "mugginess," whereas the same pressure is quite unable to saturate the atmosphere at the higher temperature of a summer day, and so it will feel quite dry and fresh. The humidity of the atmosphere is of some importance in both meteorology and industry, and is measured scientifically by the **Relative Humidity**, which is equal to

The mass of water vapour present in unit volume of the air
The mass of water vapour required to saturate unit volume
of air at its given temperature

It follows from Dalton's law of partial pressures that the water vapour exerts the same pressure as it would do if it occupied the whole space to the exclusion of the air. It has also been shown experimentally that water vapour obeys Boyle's law approximately, the deviation at the point of saturation being only 3 per cent. Except for the most accurate work, then, we may regard the density of the water vapour as proportional to its pressure. Therefore the relative humidity of the air at a given temperature may be put equal to

The actual pressure of the water vapour in the air
The pressure of water vapour needed to saturate the air at
the given temperature

74. Hygrometry.—The scientific measurement of the relative humidity of the air is called **hygrometry** and has many practical applications. Measurements of relative humidity are made at least once a day at every weather station, and it has also been shown that measurements made in aeroplanes at high altitude are of value in weather

forecasting But hygrometry has not been of great service to the meteorologist, and this application is perhaps its least important one It has, however, been put to many useful industrial applications, and recent work at the National Physical Laboratory on improved methods has attracted a great deal of attention from many branches of industry It is essential to be able to control and therefore to measure the relative humidity in a cotton mill or weaving shed, for if it becomes too low the cotton fibres get electrified by friction and will not spin satisfactorily The thread becomes uneven and the "fly waste" is greatly increased On the other hand, the humidity must not be raised above a certain value laid down by the Cotton Cloth Factories Act, otherwise the mill becomes too unhealthy to work in Another industrial application of hygrometry is furnished by cold stores in which it is necessary to control both the humidity and the temperature in order to obtain the best results The greatly increased demand for seasoned wood for the manufacture of aeroplanes at the beginning of the Great War involved the introduction of artificial seasoning and the measurement of the relative humidity of the seasoning kiln Although artificial seasoning had been adopted in America, it was never used in this country before the war The demand for high quality seasoned timber then became so pressing that natural seasoning, which occupies about two or three years, had to be abandoned for artificial seasoning which only takes a similar number of weeks The process consists of reducing the moisture content of the wood from about 50 per cent to that in equilibrium with its surroundings, about 14 per cent in this country This is done by placing the wood in a seasoning kiln, whose temperature and humidity are taken through a series of changes which are found from previous experience to season the wood without impairing its physical or structural properties. These few examples will serve to show the importance of hygrometry, and we shall now proceed to an account of the three principal methods of measuring relative humidity, the dew-point hygrometer, the wet and dry bulb hygrometer, and the hair hygrometer

75. Dew-point Hygrometers.—Dew-point hygrometers

determine the relative humidity by measuring the temperature to which the air must be cooled to deposit dew on a surface in contact with it. This temperature is called the **dew-point**. Since it has been shown experimentally that water vapour obeys Charles' law, this cooling of the air and water vapour does not alter the partial pressure of the latter. Therefore the pressure of the water vapour contained in the air is equal to the saturation pressure at the dew-point and can easily be obtained from tables once the dew-point has been determined. The saturation pressure at the actual temperature of the air can be obtained in the same way and the ratio of the one to the other gives the relative humidity.

Many different dew-point hygrometers have been designed which differ from one another in the method of cooling the surface on which the dew is to be deposited, the way in which the dew

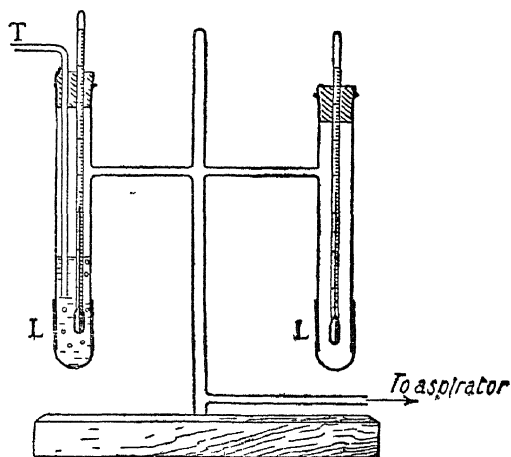


FIG 57.

is detected, and the means of measuring the temperature of the surface when the dew has been formed on it. We shall describe only one of these, the **Regnault hygrometer**, because it is the most reliable of this class of instrument, and has been adopted with slight modifications in certain industrial applications. It consists of two glass tubes, open at both ends, mounted on a suitable stand (Fig 57). A silver thimble *L* is attached to the lower end of each tube and the other end is closed by a cork pierced by a thermometer and, in the case of the left-hand tube, a narrow glass tube *T*. A little ether is poured into

the left-hand tube and is caused to evaporate by drawing bubbles of air through it by means of an aspirator joined to the tube T. This evaporation cools the ether and therefore the silver thimble and in time a deposit of dew will form on it. The temperature of the ether is read when this occurs and then the current of air is reduced so as merely to stir the ether and not to cause any appreciable evaporation. The silver thimble now begins to warm up again and the temperature at which the dew disappears is also noted. The rate of cooling should be adjusted so that these two temperatures do not differ by more than 0.5°C ; if they do, it must be reduced until the two temperatures lie within the prescribed limits, when their mean is taken as the dew-point. The purpose of the right-hand tube, through which a current of air is not drawn, is to provide a standard silver surface to compare with the one which is being cooled to enable the deposit of dew to be more readily detected. The thermometer contained in it serves to measure the temperature of the air. From the dew-point and the temperature of the air the relative humidity is calculated as described above. A simple example will serve to illustrate the principle of the method. Let us suppose that the dew-point is found to be 10°C when the temperature of the air is 14°C . From the tables we see that the saturation vapour pressure of water vapour at these two temperatures is 9.14 mm and 11.88 mm respectively. Therefore the actual pressure of the water vapour present in the air is 9.14 mm and that required to saturate it is 11.88 mm. Therefore

Relative Humidity

$$= \frac{\text{mass of water vapour present in unit volume of the air}}{\text{mass per unit volume required to saturate the air}}$$

$$= \frac{\text{actual pressure of the water vapour}}{\text{saturation pressure}} = \frac{9.14}{11.88} = 77 \text{ per cent}$$

The following features make this instrument the best dew-point hygrometer. The rate of cooling can be delicately controlled by adjusting the rate at which air bubbles through the ether. This enables the temperature of appearance and disappearance of the dew to be made as nearly

equal as possible and to be measured accurately, and also ensures the minimum difference of temperature between the ether and the outside of the silver thimble. Secondly, the method of cooling also serves to stir the ether. Lastly the appearance and disappearance of the dew is observed through a telescope which also serves to read the thermometers, thus eliminating any disturbance of the humidity of the air due to the presence of the observer. That this may be serious is shown by the fact that it requires only 13.4 grm of water vapour to saturate 1 cubic metre of air at 15° C, while the human body gives off 63 grm of water vapour per hour in repose and considerably more when taking exercise.

An industrial form of Regnault hygrometer has been designed for use in cold stores. The comparison tube is done away with and all observations are made with a telescope. The hygrometer is mounted in a tube which can be inserted through a hole in the wall of the chamber whose humidity is to be measured. A distant-reading type has also been designed in which the deposition of dew is detected by the change in reflecting power of the surface on which the dew is deposited. This is observed by the sudden decrease in deflection of a galvanometer connected to a thermopile receiving radiation which is being reflected from the surface. The temperature of the surface is measured by a thermo-couple.

The most important use of the Regnault hygrometer is to serve as a standard instrument against which other more practical types may be calibrated. It is admirably suited to this purpose, for it is capable of giving accurate results in the hands of a trained observer, and the relative humidity is calculated from the measurements according to well-established physical principles.

76. The Wet and Dry Bulb Hygrometer.—Hygrometers which are used in meteorology or industry will, more often than not, be read by observers with little scientific training and must therefore be capable of giving reliable results under these conditions. Also their accuracy must not be affected by winds or draughts. Both of these conditions at once rule out the Regnault hygrometer; it cannot be used in moving air because the ether must be cooled

considerably below the dew-point to obtain a deposit of dew from the moving air, which does not stay in contact with the silver thimble long enough to attain its temperature. The wet and dry bulb hygrometer has been designed to meet these conditions and is used at all meteorological stations. It must also be installed in cotton mills and weaving sheds by Act of Parliament.

In its original form it consists of two thermometers, one, the dry bulb thermometer, exposed to the air and the other,

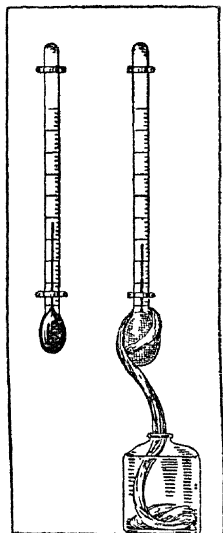


FIG 58

the wet bulb thermometer, with its bulb enclosed in a piece of muslin which is kept saturated with water by a piece of wick reaching to a reservoir full of water (Fig 58). The full details of the mounting of the muslin, wick, and reservoir can be obtained from the *Observer's Handbook*, published by the Meteorological Office, and must be carefully observed if the results are to be of any value. The dry bulb gives the temperature of the air, but the wet bulb thermometer will usually read lower than this because of the evaporation of the water from the muslin surrounding it. The latent heat needed for this is absorbed from the bulb of the thermometer and causes it to register a temperature lower than that of the surrounding air. The greater the relative humidity, the slower this evaporation will be, and therefore the less the difference in

temperature between the wet and dry bulbs. When the relative humidity is 100 per cent, no evaporation will occur and so the difference in temperature will be zero. Since there is some connection, then, between the difference in temperature of the wet and dry bulbs and the hygrometric state of the atmosphere, it should be possible to deduce the relative humidity from the readings of the wet and dry bulbs.

Tables have, in fact, been drawn up from which the

relative humidity can be read off when the wet and dry bulb temperatures are known. It has been found that the ordinary wet and dry bulb hygrometer has one serious defect, in that the reading of the wet bulb depends on the speed with which the air is flowing past it. Further investigation led to the discovery that the reading was independent of the velocity of the air provided that it is greater than 4 metres per second. This led to the introduction of the **ventilated wet and dry bulb hygrometer**, in which a stream of air is drawn past the thermometers at a speed greater than 4 metres per second. The commonest type is the Assmann psychrometer, in which this is done by clockwork-driven fans.

This instrument, when compared with a dew-point hygrometer as standard, gives results consistent to 1 or 2 per cent over a wide range of humidities and at temperatures below 0°C . The unventilated wet and dry bulb hygrometer, on the other hand, can hardly be relied on to 5 per cent.

Although some form of ventilated wet and dry bulb hygrometer is in common use in America, it has not yet been introduced in this country to any great extent. Both in meteorology and in industry it is felt that the unventilated type gives results as accurate as can be expected from untrained observers and indeed as accurate as is necessary for their purpose. Their use in weaving sheds by Act of Parliament, for example, is purely empirical. Two or more hygrometers must be mounted in every shed and must be read three times a day between specified times. It is laid down that artificial humidification must cease at a wet bulb temperature of 72.5°F and that all work shall cease if the wet bulb temperature rises to 80°F .

77. The Hair Hygrometer.—The hair hygrometer seems at first sight to be the most useful of all in practice, since it can be made into a pointer or direct reading instrument. Its mode of action depends on the facts that hair is hygroscopic and when a piece of hair kept under tension by a spring absorbs moisture its length increases. Since the amount of moisture absorbed by the hair and the consequent increase in length depends on the relative humidity of the atmosphere, if the elongation is magnified by a

suitable device so as to move a pointer over a scale, the position of the pointer indicates the length of the hair and is therefore a measure of the relative humidity of the atmosphere. In fact the scale, can be calibrated directly in relative humidity by comparison with a dew-point hygrometer. We shall not enter into any further details of the construction of the hair hygrometer here as the different types only differ from one another in the device for magnifying the elongation, which is of no fundamental importance. We may conclude, however, by mentioning that it is important to see that the hair is free from grease, otherwise this interferes with the absorption of moisture and renders the instrument quite untrustworthy.

The first hair hygrometer was invented by de Saussure in 1783, but these instruments earned the reputation of being unreliable. As the evidence on which this view was based did not appear to be conclusive, Dr Griffiths, of the National Physical Laboratory, decided to carry out a systematic investigation of the accuracy and reliability of the instrument under a wide range of humidities and temperatures, with a view to seeing if it would be suitable for use in cold stores. He came to the following conclusions :

(a) The hygrometer tends to read too high as time elapses, owing to the hair acquiring a permanent increase in length.

(b) The most reliable instruments are those in which the hair is subjected to the minimum tension.

(c) The calibration of the instrument should be checked at frequent intervals under conditions identical with those under which it is used. Its readings can then be relied upon to less than 3 per cent.

The hair hygrometer has been used for the measurement of the humidity of cold stores and is particularly suitable for temperatures below 0°C . As the unventilated wet and dry bulb hygrometer is of very little use at such temperatures, it has been suggested that it should be replaced by the hair hygrometer at meteorological stations when the temperature is under 0°C .

78. Other Hygrometers.—We shall conclude this outline of the measurement of relative humidity by mentioning one or two other hygrometers which have been used. The **chemical hygrometer** measures the relative humidity

directly ; the mass of water vapour in a measured volume of the air is found by drawing the air through a series of drying tubes and finding the consequent increase in mass. The mass of water vapour required to saturate the same volume of air at the same temperature can either be read off from tables or determined in the same way by substituting artificially saturated air for the actual air. The ratio of the mass of water vapour present in the given volume of air to the mass required to saturate the same volume at the same temperature is the relative humidity. The method is tedious, as it takes quite half an hour to draw the sample of air through the drying tubes, and it has the additional disadvantage that it only gives the average humidity of the air during that time. Its only use is to serve as a standard with reference to which other hygrometers can be calibrated ; it is probably no more accurate, and certainly less convenient, than the dew-point hygrometer, which is therefore equally satisfactory for purposes of calibration. For that reason the chemical hygrometer is not described in any great detail in this book.

The **absorption hygrometer** measures the pressure of the water vapour present in the atmosphere directly by finding the decrease in pressure in an enclosed mass of air due to the absorption of the water vapour by a drying agent. A suitable form has been designed for use in cold stores.

The **thermal hygrometer** depends for its action on the fact that a thermometer whose bulb is enclosed in dry cotton wool suffers a rise in temperature on being exposed to a humid atmosphere. This is due to the fact that the dry cotton absorbs some of the water vapour, which gives up its latent heat on condensing. Further details of these hygrometers and those which have been described previously can be obtained from "A Discussion on Hygrometry," published in the *Proceedings of the Physical Society of London*, Volume 34, Part 2, February 15th, 1922. The modern developments in hygrometry given in this chapter have been obtained from the same source, and the author accordingly wishes to acknowledge his indebtedness to the Physical Society for the publication of this discussion.

EXAMPLES ON CHAPTER VII

1 Explain clearly what is meant by a saturated vapour. Describe how you would measure the vapour pressure of water (a) at temperatures below its freezing point, (b) at temperatures above its boiling point. Emphasise in each case the physical principles on which the method is based.

2 How would you measure the vapour pressure of a liquid at different temperatures?

A mixture of gas and a saturated vapour is contained in a closed space. How will the pressure of the mixture vary (a) when the temperature is changed and the volume is kept constant, (b) when the volume is changed and the temperature is kept constant? (*O and C*)

3 Describe an experiment to determine the saturation pressure of ether vapour at temperatures in the neighbourhood of that of the room.

The gas tube of a Boyle's law apparatus is provided with a tap through which small quantities of liquid can be admitted into the tube. Initially the tube contains 25 c.c. of dry air, the level of the mercury in the reservoir being 33 cm. below that in the gas tube. A very small quantity of ether is then admitted so that the volume becomes 35 c.c. and the difference in the mercury levels 17 cm. The barometric pressure is 75 cm. and the saturation pressure of ether vapour at the temperature of the tube 49 cm. Find how the volume of the space containing the air and vapour must be altered so that it may just become saturated. (Assume that the unsaturated vapour obeys Boyle's law) (*N U J B*)

4 Explain what is meant by saturation vapour pressure. The saturation pressure of water vapour varies between 93°C and 100°C by 24.5 mm. of mercury per degree. Find the height above sea-level of a hut where water is found to boil at 93°C if the density of air at sea-level is 0.013 gm. per c.c. The variation of temperature may be neglected. Pressure at sea-level = 10^6 dynes per sq. cm. (*Camb Schol*)

5 What are the principal differences between saturated and unsaturated vapours?

How would you determine the pressure of saturated water vapour at temperatures between 40°C and 110°C ? (*Camb Schol*)

6 Describe a method suitable for the determination of the density of a gas such as hydrogen.

What percentage error would be introduced by the presence of 1 per cent. by volume of nitrogen as an impurity?

7 Discuss the evidence on the deviation of vapours from Boyle's law

8 What is meant by (a) relative humidity, (b) dew-point?

Describe in detail the modern form of Regnault's hygrometer, and discuss the part it plays in the practical measurement of relative humidity

9 What is meant by the hygrometric state of the air? Describe a satisfactory way of finding it

Calculate what fraction of the mass of the water vapour in the air would condense if the temperature of the air fell from 20°C to 5°C , and if originally, at 20°C , the humidity was 60 per cent

Saturation pressure of water vapour at $20^{\circ}\text{C} = 17.5\text{ mm}$; at $5^{\circ}\text{C} = 6.5\text{ mm}$ (N U J B)

10 Explain the general principles underlying the employment of a wet and dry bulb hygrometer for determining the hygrometric state of the atmosphere, explaining carefully what is meant by hygrometric state

11 Describe the hair hygrometer, and discuss the industrial applications of hygrometry

12 The air near the ground in the neighbourhood of an aerodrome is saturated at 15°C , when the pressure of the water vapour is 1.2 cm of mercury. In the evening the air cools down to 5°C , when the saturation pressure of the water vapour is 0.65 cm, and a fog is produced. Calculate the mass of water vapour which condenses to water in each cubic foot of the atmosphere, given that 1 gram of saturated steam occupies 1650 c.c. at 100°C and 76 cm pressure and that water vapour obeys Boyle's and Charles' laws right up to the point of saturation

If it is necessary to clear the fog over a square of side 400 yards to enable aeroplanes to land, calculate the amount of heat needed to do this if the fog is 100 feet high and the latent heat of vaporisation of water at 5°C is 596 cal per gram. Calculate the cost if the calorific value of the coal from which the heat is ultimately derived is 8000 cal per gram and the cost of the coal is 8d per kilogram. Assume that 50 per cent of the heat generated by the coal is wasted

CHAPTER VIII

THE DYNAMICAL THEORY OF HEAT

79. The Caloric Theory of Heat.—We have so far confined ourselves to collecting a considerable body of experimental facts concerning heat and the associated phenomena, and it is now time to pause with a view to forming some theory to explain these facts that they may be the better correlated and understood, and that our search for new facts may be guided into fruitful channels. At the moment we shall be well advised to confine ourselves to the fundamental facts requiring explanation, which may be summed up as follows

(a) Heat is conserved; that is, whenever there is an exchange of heat between two or more bodies, it is found that the total amount lost is always equal to that gained

(b) Bodies expand when they are heated

(c) The change of state from solid to liquid or liquid to gas is invariably accompanied by an absorption of heat without a rise in temperature.

From the very earliest times there have always been two rival theories of heat, the one contending that heat is some kind of motion and the other asserting that it is a fluid. The latter view gained the most favour, and was generally accepted up to the beginning of the nineteenth century.

According to this theory, heat is a self-repellent fluid, called **caloric**, which raises the temperature of any body to which it is added, and lowers that of any body from which it is removed. It is postulated that it is impossible to create or destroy caloric, and this at once explains the first fact mentioned above. The expansion of bodies with rise in temperature is explained in this way. When a body is heated, caloric is added to it, and fills the interstices of the body. Since the fluid is self-repellent, it will drive the ultimate particles of the body further apart, and so cause it to expand. The absorption of latent heat without any rise in temperature accompanying a change in state is very ingeniously explained by supposing that the caloric and the solid, say, form a *kind of chemical compound*, the liquid,

which therefore has its own properties and does not exhibit those of either constituent. Thus the properties of the caloric are suppressed, and it does not produce any rise in temperature.

80. The Downfall of the Caloric Theory.—The first hint that all was not well with the caloric theory came as a result of some experiments by Count Rumford, an artillery engineer. He was engaged in boring the barrel of a cannon, and noticed that the chips of steel cut off by the boring tool were very hot. The necessary heat cannot come from the surroundings, since the temperature of the outside of the cannon is less than that of the inside. On considering the matter further, he found it rather difficult to account for the source of this heat, and posed this question to the supporters of the caloric theory. Their explanation was not only ingenious, but had the further merit of lending itself to experimental test. It is known that different substances have different capacities for heat, or different specific heats as we should say, and they asserted that the specific heat of iron in the powdered state was less than that in bulk. It follows at once that when iron is broken up into the powdered state, a rise in temperature will occur *without the addition of any heat*. It should be noticed that this explanation removes Rumford's difficulty, for there is no more heat in the powdered iron than there was before it was broken up. Without waiting to see if their assumption that the specific heat of a substance in the powdered state is less than that in bulk was verified by experiment, Rumford proceeded to embarrass the supporters of the caloric theory still further by repeating his experiment with a blunt borer. In this way he was able to raise 100 lbs. of cold water to the boil in $2\frac{1}{2}$ hours while producing but a few grams of iron filings. It is difficult to believe that such a large amount of heat could be produced by the decrease in thermal capacity of such a small quantity of iron and the position becomes impossible when it is added that *the supply of heat showed no signs of giving out at the end of the $2\frac{1}{2}$ hours, and is apparently inexhaustible*. The position of the supporters of the caloric theory was finally rendered untenable by subjecting their fundamental assumption to the test of experiment, when it was found that there is no

difference in the specific heat of a substance in the powdered state and in bulk

Although the experimental facts were against them, the calorists still clung to their theory with that conservatism that is innate in human nature and so Davy (afterwards Sir Humphrey Davy) planned another crucial experiment in an attempt to convince them of their error. He mounted two pieces of ice suitably and rubbed them together for some time. He succeeded in this way in melting very nearly all the ice, and he noticed that the melting was confined to the two surfaces in contact. He did not touch the ice with his hands, so the necessary latent heat could not have come from them, and he showed by a subsidiary experiment that it could not come from any of the bodies in contact with the ice. The supporters of the caloric theory admit that an absolute quantity of heat is added to ice when it melts; where has that heat come from in this experiment? We have shown that it has not come from the surroundings. Their explanation of the rise in temperature in Rumford's experiments does not apply here for two reasons; firstly, the whole point of that explanation is that the amount of heat in the system remains constant, which is certainly not the case here, secondly, it requires that the specific heat of the body shall be less after the rubbing than it was before, whereas the specific heat of water is twice that of ice! The caloric theory has completely broken down before this experimental fact, which ultimately led to its abandonment. Its fate is a common one, for the path of Science is freely strewn with discarded theories. Science admits no theory which is unable to offer a satisfactory explanation of the facts. Such a theory may survive for a time, but its ultimate rejection is inevitable.

We may digress at this point for a moment to consider precisely what is meant by the term "satisfactory explanation" used above. The reader may be inclined to object to the adjective "satisfactory" on the ground that it introduces a disappointing element of uncertainty into scientific knowledge. It is frequently asserted that the value of scientific knowledge is its certainty, it may not be fundamental, but it is certain and definite, provided that

the underlying concepts of the subject, such as space and time in Physics, are not questioned. This certainty is based on the supposition that there is only one theory that will explain a given set of experimental facts. This is not true, probably the caloric theory could be so modified as to explain the experiments of Rumford and Davy, but it would have to be so transformed in the process and so many assumptions would have to be introduced, that the explanation would give no æsthetic satisfaction to the mind. It is important to realise, then, that there is a personal element even in Science, and that the ultimate criterion in deciding between two theories both of which explain the facts is æsthetic. The theory chosen is the one which gives the greater intellectual satisfaction, the one which is the more beautiful. The process is not logical, but intuitive.

81. Joule's Experiments on Heat as a Form of Energy.—Although Rumford's experiments were done in 1798 and those of Davy in 1812, the belief in the truth of the caloric theory still persisted. This induced Joule, who was convinced that heat was a form of energy, to undertake a series of experiments to put the matter beyond all possible doubt. He was led to his conviction concerning the nature of heat by seeing that the feature common to both Rumford's and Davy's experiments was that *mechanical work was being done*, in the one case by the borer against the friction of the inside of the cannon and in the other by the two pieces of ice against each other. It then occurred to him that this mechanical work was the source of the heat which was produced, and he saw, moreover, that the supply would be inexhaustible as appeared likely from Rumford's experiments.

Joule saw that the way to obtain a decisive proof of the truth of his view was to put the matter on a quantitative basis, and show that when a given amount of mechanical work is done the same quantity of heat is always produced. This forms yet another good example of the celebrated saying of Lord Kelvin quoted in Art 9. In Science we always aim at measuring things in numbers, because the information is necessarily more precise and because it enables us to make use of the logic of mathematics. If the reader will recall the different quantities which we

have so far considered, such as temperature, quantity of heat, expansion, vapour pressure, and so on, he will remember that every one has been measured in numbers, and he will realise that most of the information which we have obtained about them could not have been discovered if we had not been able to measure them in this way

Joule's plan of work went even further than this. He foresaw the possibility that a certain fraction of the work done might be converted into some form of energy other than heat, of which the experiments would take no account, and he realised that this would not be detected if the work was always done in the same way, as the fraction lost would always be the same. So he saw that it was necessary to make arrangements to do the work in various ways, so that the fraction lost might be given a chance to vary, and see if a given amount of work always produced the same quantity of heat in all cases. Even then there is just the possibility that the fraction of work lost does not alter when the method of doing the work alters. To prove that all the work done is being converted into heat it is necessary to reverse the process; that is, some kind of engine must be used to convert heat into work and the amount of work obtained from the disappearance of a given quantity of heat corrected for radiation and other losses must be measured. If it is found that, however the mechanical work is done, a given amount of work always produces the same amount of heat, and that the disappearance of that same quantity of heat produces the given amount of mechanical work, then it is certain that all the work is being converted into heat and that heat is a form of energy. We shall now proceed to describe one of Joule's experiments in some detail and then give a list of the others with the result obtained in each case.

The principle of Joule's first experiment was to measure the amount of work done against the friction of a brass paddle turning in water and to determine the heat produced by the rise in temperature of the water. His apparatus is illustrated in Figs 59 and 60. The calorimeter is closed by a lid containing two holes, one for the axle of the paddle and the other for the insertion of a thermometer to read the temperature of the water and calorimeter. The

paddle is made of brass, and heat is prevented from escaping from it by means of the boxwood cylinder B. It is connected to a cylinder, which can be rotated by the weights G joined to it by string passing over two pulleys. The paddle consists of eight sets of four arms spaced equally round the axle and rotating in between four sets of vanes, each having five arms fixed to the wall of the calorimeter.

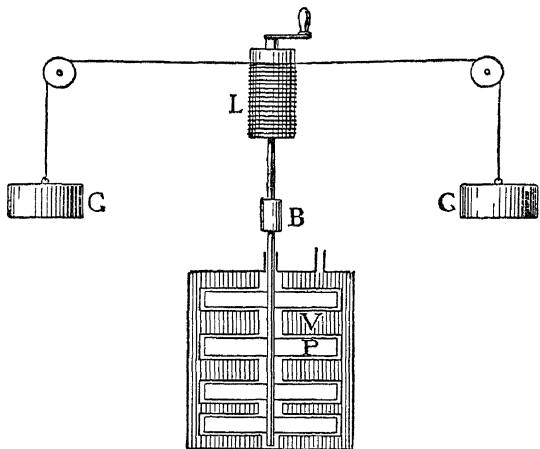


FIG 59

The procedure in an experiment is as follows. After weighing the paddle and the calorimeter empty and filled with a convenient volume of water, the paddle is inserted in the calorimeter with the weights wound up and the lid of the calorimeter is put on. After the temperature of the water has been read, the thermometer is removed and the weights are allowed to fall

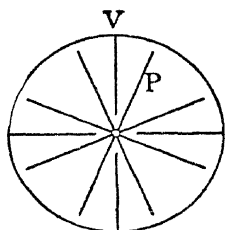


FIG 60

through a measured distance. The cylinder L is disconnected from the axle of the paddle, thus allowing the weights to be quickly wound up again without rotating the paddle, after which the cylinder is connected to the paddle once more and the weights are allowed to fall again. This is repeated from ten to twenty times until a convenient rise in temperature has been obtained, one complete experiment occupying about an hour. The rise in temperature is measured by taking the temperature at the end of the whole experiment.

If M is the mass of each weight and h is the height through which they fall n times, then the work done is $2nMgh$ ergs, g being the acceleration of gravity. If W is the water equivalent of the calorimeter and its contents, and t_1 and t_2 the initial and final temperatures, the heat developed is $W(t_2 - t_1)$ calories. If J is the amount of work needed to produce the unit quantity of heat, that is the mechanical equivalent of heat, then

$$JW(t_2 - t_1) = 2nMgh$$

As all the quantities in this equation are known except J , it can at once be calculated.

Since the rise in temperature in this experiment was rather less than 1°F in one hour, the cooling correction is comparable with the rise in temperature due to the work done, and must therefore be determined accurately. Joule did this by finding the loss in temperature of the calorimeter each time the weights were being wound up, and by noting the time occupied in the winding up he was able to calculate the average rate of loss of heat during the whole experiment. The product of this and the total time during which heat was being produced by the rotation of the paddles is equal to the correction to be added to the measured rise of temperature to obtain that which would have occurred in the absence of cooling. Joule also corrected for the kinetic energy of the weights on reaching the ground and the friction of the string on the pulleys. In fact this experiment, and indeed the whole series, was carried out with an eye to the essential points, and yet with an attention to detail, which entitles it to a place among those classic experiments, which are models of what a scientific determination should be.

82. Further Experiments.—Joule's second and third set of experiments were performed on the same lines as those described above, but the water was replaced by mercury and the paddle and vanes were made of iron. In his fourth and fifth set of experiments heat was produced by the friction of two iron rings rubbing against one another immersed in mercury. In another set of experiments the work was done by forcing water through narrow tubes, and in a further set the heat produced by compressing a given

mass of gas was measured. Finally, Joule designed an electrical method of producing heat, and obtained a value of the mechanical equivalent of heat from this set of experiments. The results he obtained by the different methods are shown in Table VI

TABLE VI

Method.	The number of Ergs in x Calorie
Friction between brass paddles and water	$4\ 161 \times 10^7$
Friction between iron paddles and mercury	$4\ 169 \times 10^7$
Friction between iron rings in mercury .	$4\ 174 \times 10^7$
Forcing water through narrow tubes .	$4\ 168 \times 10^7$
Compression of air	$4\ 36 \times 10^7$
Electrical method	$4\ 52 \times 10^7$

These values agree with one another to within the limits of experimental error, the comparatively large divergence of the last two being due to the fact that the corresponding methods were not capable of yielding accurate results for various reasons into which we cannot enter here. These experiments, then, establish the fact that there is a definite relation between work, as such, and heat, which is independent of the way in which the work is done and so make it certain that heat is a form of energy.

Hirn performed some quantitative experiments on the converse process just to make quite sure that all the work is being converted into heat in Joule's experiments. He measured the quantity of heat supplied to a steam engine in a given time, and also the quantity rejected in the same time. He also estimated the quantity of heat lost in cooling, and other causes, and this subtracted from the difference of the heat supplied and that rejected gives the amount which was converted into work. He measured the amount

of work done by the engine in the given time, and so was able to calculate the number of ergs of work obtained when 1 calorie of heat disappears. Considering the difficulty of his experiment his result, 4.18×10^7 ergs per calorie, agrees very well with Joule's values, and proves conclusively that heat is a form of energy and that when work is done all of it is converted into heat, and that none is transformed into some hitherto unknown form of energy.

83. Mayer's Work on the Equivalence of Heat and Energy.—While Joule had been carrying out this experimental work, Mayer had arrived at a value of the number of ergs in 1 calorie by reasoning based on the difference in the two specific heats of a gas. We have already seen (Art 18) that the specific heat of a gas at constant pressure is greater than that at constant volume; Meyer suggested that this is due to the fact that when the gas is heated at constant pressure it expands, and so heat must be supplied not only to raise the temperature of the gas but also to do the external work against the atmospheric pressure in expanding. He then proceeded to derive an expression for the difference of the two specific heats in the following way. Let us suppose that unit mass of the gas is heated through a temperature dT at constant volume, the heat required is $C_v dT$, where C_v is the specific heat of the gas at constant volume. If the gas now suffers the same rise of temperature at constant pressure p , the heat required $C_p dT$ is given by

$$C_p dT = C_v dT + p \cdot dv, \quad . \quad (42)$$

where dv = the increase in volume of unit mass of the gas due to a rise in temperature dT at constant pressure, and C_p = the specific heat of the gas at constant pressure. Assuming that the gas obeys the ideal gas equation, as all gases do under ordinary conditions, we have

$$pv = rT,$$

where r = the gas constant for unit mass of gas

Differentiating this equation, and bearing in mind that the pressure is constant, we have

$$p \cdot dv = r \cdot dT.$$

Substituting this value of $p \cdot dv$ in equation (42), we have

$$C_p - C_v = r \quad . \quad . \quad . \quad (43)$$

Now C_p and C_v are measured experimentally in calories per gram per $^{\circ}\text{C}$, and r can only be calculated in ergs per gram per $^{\circ}\text{C}$ from the gas equation. So this equation will give the number of ergs in 1 calorie.

We shall now proceed to calculate this number by considering the case of hydrogen. For this gas,

$$\begin{aligned} C_p &= 3.4 \text{ calories per gram per } ^{\circ}\text{C}, \\ C_v &= 2.4 \text{ calories per gram per } ^{\circ}\text{C}. \end{aligned}$$

We have already calculated r for hydrogen (Art. 48), and obtained the value 4.13×10^7 ergs per gram per $^{\circ}\text{C}$.

From equation (43) it follows at once that

$$1 \text{ calorie} = 4.13 \times 10^7 \text{ ergs}$$

The agreement between this value and those obtained experimentally by Joule and Hirn is very satisfactory, especially bearing in mind that the equation on which the calculation is based is only true for an ideal gas, and it is quite possible that this is not the case for hydrogen.

We may sum up all this work by saying that there is a real relation between heat and work, which is independent of the way in which the work is done or whether the conversion is from work into heat or the opposite way round. It is, in fact, established that heat is a form of energy.

One further problem remains for solution, it is of practical rather than theoretical importance. It is the determination, with the greatest possible precision, of the number of ergs in 1 calorie, which is called the mechanical equivalent of heat and will be denoted by the letter J . But it must be emphasised that this is of the same nature as the determination of the number of centimetres in an inch; it is a conversion factor, for heat is a form of energy, and quantity of heat can be measured either in ergs or calories; and equally well energy can be expressed in calories as well as in ergs.

84. Rowland's Determination of J .—Joule considered that the method of developing heat by the friction of paddles rotating in a liquid gave the most accurate value for the

mechanical equivalent of heat of those that he tried. So in 1879 Rowland decided to carry out a determination of the mechanical equivalent of heat by this method aiming at an accuracy of 1 in 2000. He saw that Joule's experiments were open to two objections

(a) The rate of rise of temperature, about 1°F per hour, was so small that the cooling correction formed too large a proportion of the total rise in temperature, which therefore could not be accurately found

(b) Joule's mercury thermometers were not corrected to any standard scale of temperature, such as the constant volume hydrogen scale, and so his rises in temperature were measured on an arbitrary scale, whose relation to a standard scale could not now be determined, as the thermometers were no longer available.

Joule himself was aware of the first of these objections and had designed an apparatus in 1878, at the request of the British Association, in which the rate of rise of temperature was some thirty times greater.

Rowland's apparatus and method are based on the same principle as that used by Joule in his 1878 experiments, but are so improved as to give an even bigger rate of rise of temperature, namely, 35°C per hour. He overcame the second objection to Joule's earlier experiments by correcting his mercury thermometers to a standard gas scale of temperature

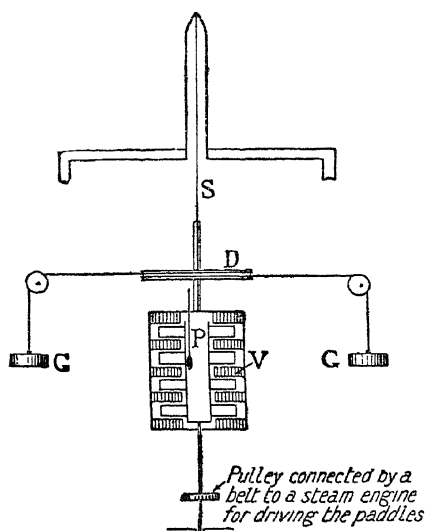


FIG 61.

His apparatus consisted of a calorimeter fitted with a set of vanes *V* suspended by a torsion wire *S* (Fig 61).

A set of paddles P was made to rotate inside the calorimeter by a steam engine attached by a belt to a pulley on the axle of the paddles, which emerges from the bottom of the calorimeter. The friction between the paddles and the calorimeter tends to rotate it from the equilibrium position, to which it is restored by the couple exerted by the weights GG attached to the drum D. The work done against this couple by the rotating paddles is converted into heat and causes a rise in temperature of the calorimeter and its contents. The system of paddles and vanes is very much more elaborate than in Joule's experiments in order to produce more friction, and so a greater rate of rise in temperature, and also to ensure a thorough mixing of the water.

The procedure in an experiment is as follows. The calorimeter is weighed empty, filled with a suitable amount of water and weighed again, the paddles are also weighed. The apparatus is then assembled and the temperature of the water is read. The engine is now started up and the paddles are set rotating, and the weights GG are immediately adjusted so as to keep the calorimeter in its equilibrium position. The paddles are rotated until a convenient rise in temperature has been obtained, the number of revolutions being recorded by a counter, and the temperature being read at frequent intervals. In this way a considerable number of readings of the number of revolutions of the paddle and the corresponding rise in temperature are obtained, from any pair of which J can be calculated. If the paddle makes n revolutions against the couple due to the two masses M acting on a drum of diameter d and raises the temperature of the calorimeter and contents, whose water equivalent is W, from t_1 to t_2 , the work done by the paddles against the frictional couple $= 2\pi n Mgd$ and the heat produced by this work $= W(t_2 - t_1)$

$$\therefore J \cdot W(t_2 - t_1) = 2\pi n Mgd$$

from which J can at once be calculated

The cooling correction was determined by allowing the calorimeter to cool with the paddles turning slowly to stir the water. The heat produced by this stirring was calculated and allowed for.

Rowland himself reduced his temperature readings to the constant volume air scale, but his mercury thermometers were afterwards compared with some standardised on the constant volume hydrogen scale and this enabled his results to be reduced to the constant volume hydrogen scale. They are shown in the following table, which gives the number of ergs required to raise the temperature of 1 grm of water through 1°C at various temperatures:

TABLE VII

Temperature in $^{\circ}\text{C}$.	Number of Ergs required to raise 1 grm of Water through 1°C
10	$4\ 196 \times 10^7$
15	$4\ 188 \times 10^7$
20	$4\ 181 \times 10^7$
25	$4\ 176 \times 10^7$
30	$4\ 174 \times 10^7$
35	$4\ 175 \times 10^7$

The *regular* variation of the number of ergs with temperature implies that the specific heat of water varies with temperature and also raises the question of the definition of the calorie. This has so far been defined as the amount of heat needed to raise 1 grm of water through 1°C . But these experiments have shown that this is not a constant quantity, that rather less heat is required to raise 1 grm of water from 30°C to 31°C than from 15°C to 16°C . It is therefore necessary to specify the precise range of temperature in defining the calorie. Before coming to any decision it will be as well to confirm Rowland's results by other methods, and so a discussion of this matter will be postponed until these methods have been described.

We may notice in passing that in 1930, just over fifty years since Joule performed his 1878 experiments on J , they have received a practical application, which may be of far-reaching importance. Engineers have tried without success to harness the energy of the tides for a long time, the chief difficulty on the commercial scale being that the supply is not continuous. A demonstration plant has now been erected at Avonmouth Dock, Bristol, in which a portion of the energy generated when the water level sinks after high tide is made to drive a water friction brake,

which is identical with Joule's or Rowland's apparatus for J . The water in the friction brake is thus raised to a high temperature and is stored in a vessel at high pressure, from which it can be drawn off as steam to work an electric generator during the periods when the supply of energy from the tides is too small to work the water turbines.

85. Callendar and Barnes' Electrical Method for J .—The electrical method of determining the mechanical equivalent of heat, which was first used by Joule, consists in heating up some water by the passage of an electric current through a wire immersed in it. The electrical energy dissipated is measured in ergs and the heat produced in calories, and so the number of ergs in one calorie can at once be calculated. The method has been tried by several workers, and perhaps the most accurate results were obtained by Callendar and Barnes, whose experiments had

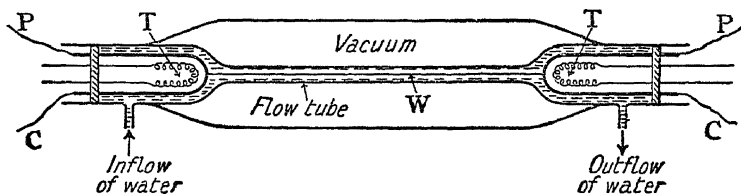


FIG 62

the additional advantage of employing the method of continuous flow calorimetry, the principle of which has already been explained in connection with the determination of the specific heat of a gas at constant pressure (Art. 21). It should be stated in fairness that, although Callendar suggested the method and designed the apparatus, the actual experiments were carried out by Dr Barnes alone.

The apparatus consists of a thin platinum wire W , secured at each end to a thick copper tube and mounted inside a glass tube through which there is a steady flow of water (Fig 62). The platinum wire is heated by an electric current led in by the current leads CC , the potential leads PP being used for measuring the $P D$ across the wire. Consequently, the water is heated up as it flows along the platinum wire and leaves the apparatus at a higher temperature than that at which it entered. The thick copper

tubes, which develop a quite negligible amount of heat, serve to communicate the temperature of the inflowing and outflowing water to the platinum resistance thermometers TT. The flow tube is surrounded by a vacuum to reduce the cooling correction to a minimum, and this in turn is surrounded by a water jacket kept at a constant temperature (not shown in the diagram). The experiment is begun by turning on the electric current and the flow of water. When sufficient time has elapsed to allow a steady state to be attained, the platinum resistance thermometers are read and the mass of water flowing through the apparatus in a given time is measured, the time being obtained from an electric chronograph reading to 0.01 sec. In a typical experiment 500 grms of water flows through the apparatus in 15 mins, and undergoes a rise in temperature of 8°C , which is measured to $\frac{1}{10000}^{\circ}\text{C}$ by the platinum resistance thermometers. The potential difference between the ends of the wire is measured by a potentiometer and a standard Clark cell, and the current is calculated by measuring the potential difference across a standard 1 ohm resistance in series with the wire. The standard Clark cell is a specially constructed cell whose E.M.F. remains constant to 1 in 10,000, and is known in volts to the same order of accuracy. The P.D. across the ends of the platinum wire is compared with the E.M.F. of the Clark cell by the potentiometer, and knowing the E.M.F. of the cell the required P.D. can at once be calculated. It must be emphasised here that the E.M.F. of the cell must be accurately known in true volts; it is useless to measure it with a voltmeter, for example, since the calibration may be incorrect. It is usual to measure it by an absolute method, that is, one based on the definition itself and not requiring the knowledge of any other P.D. In the same way, the value of the standard resistance must be accurately known from an absolute determination, the current being given by the ratio of the P.D. across it to the resistance. The reason for an accurate knowledge of these standards will be understood when it is realised that the volt is *defined* as the P.D. through which a coulomb must fall in order to dissipate one joule of electrical energy. Therefore, the number of joules of electrical energy dissipated will not be known accurately if the value of

the P.D. across the wire and the current through it are not known accurately also

If M grms of water flow through the apparatus in t secs and rise in temperature from $\theta_1^\circ \text{C}$ to $\theta_2^\circ \text{C}$, while the P.D. across the platinum wire and the current through it are V volts and C amps respectively, we have

$$M(\theta_2 - \theta_1)J = V Ct \times 10^7 + H,$$

where H is the heat lost by cooling in time t secs measured in ergs, and J is the number of ergs required to raise 1 grm of water at $\frac{\theta_1 + \theta_2}{2}^\circ \text{C}$ through 1°C . The cooling correction, H , which is small in any case, is eliminated by repeating the experiment using different values of V , C , and M , but the same values of θ_1 , θ_2 , and t . Consequently, the value of H and J are the same for the two experiments, and we have two equations from which these two unknowns can be calculated

The advantages of the continuous flow method of calorimetry have already been enumerated in connection with the determination of the specific heat of a gas at constant pressure (Art 21), but it will be as well to reiterate them here. The essential feature of the method is that all temperatures are steady while measurements are being made, and so

- (a) the thermal capacity of the calorimeter is eliminated,
- (b) the temperatures can be measured to $\frac{1}{10000}^\circ \text{C}$, a much higher degree of accuracy than could be obtained if they were varying,
- (c) the rate of loss of heat due to cooling is constant, and so can be determined more accurately than if the temperature of the calorimeter is changing

The result of these experiments was that it requires 4.182×10^7 ergs to raise 1 grm of water at 15°C through 1°C . It will be seen that this result differs from Rowland's value for J by more than the experimental error of either determination and so it was essential to carry out yet another determination aiming at an accuracy of 1 in 10,000. This was undertaken by **Laby and Hercus** in 1927, and their result was $J = 4.186 \times 10^7$ ergs to raise 1 grm of

water at 15°C . through 1°C , which is in very close agreement with the mean of the values obtained by Rowland and Callendar and Barnes, and is accepted as the most accurate value of J so far obtained. Any reader who is interested in the method used by Laby and Hercus should consult *Heat and Thermodynamics*, by J K Roberts, where an account of their experiments is given.

86. The Variation of the Specific Heat of Water with Temperature.—We have already seen that Rowland's experiments show that the specific heat of water varies with temperature and therefore necessitate a revision of our definition of the calorie. It would obviously be unwise to come to any final decision on this point until Rowland's results have been confirmed by other methods, but for the sake of simplicity in describing such methods we shall make a tentative definition. We shall call this unit **the 15°C . calorie** and define it to be the amount of heat required to raise 1 grm of water from 14.5°C to 15.5°C .

Callendar and Barnes' continuous flow method for J was used for an investigation of the variation of the specific heat of water with temperature. It is merely necessary to find the rise in temperature produced in a given mass of water by a given quantity of electrical energy at various temperatures. The rise in temperature is kept down to 8°C , and the ratio of the rises in temperature at two given temperatures is inversely as the ratio of the specific heats of water at those temperatures. Since we only need to know that the rate of supply of electrical energy is constant, but do not need to know its value in joules, there is no necessity to know the E.M.F. of the Clark cell in volts and the value of the standard resistance in ohms, which, in Callendar's opinion, were the least accurate of the measurements in the determination of J . So these experiments are more accurate than those to find J , since they do not include these uncertain quantities.

Callendar and Barnes' results are shown in the following table taken from Roberts' *Heat and Thermodynamics*, the specific heat being measured in 15°C calories per grm. per $^{\circ}\text{C}$.

It will be seen at once that there is a definite discrepancy between Rowland's and Callendar and Barnes' results;

TABLE VIII

Temperature in °C	Specific Heat	Temperature in °C.	Specific Heat
5	1 0047	35	0 9973
10	1 0019	40	0 9973
15	1 0000	50	0 9978
20	0 9988	70	1 0000
25	0 9980	90	1 0036
30	0 9976	100	1 0057

for instance, the former finds the minimum specific heat at 30° C whereas the latter finds it at 37° C. It is obviously most important to settle which of the two results is the more reliable and so Callendar devised another way of finding the specific heat of water at various temperatures depending on the method of mixtures

87. Callendar's Continuous Mixture Method.—This method is really a most ingenious combination of the method

of mixtures and the continuous flow method. A current of air-free water flows at a steady rate through the closed circulating system shown in Fig 63. It emerges from the **heater**, which is kept at a constant temperature, and flows on to the **exchanger**, which it enters at a temperature θ_4 , about 100° C, and leaves at a temperature θ_3 , about 70° C. It

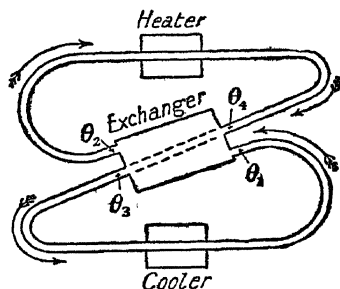


FIG 63

then passes on through the **cooler**, which is maintained at a constant temperature and serves to decrease the temperature of the stream of water still further, and returns to the exchanger, which raises its temperature from θ_1 , about 30° C, to θ_2 , about 60° C. After passing through the exchanger, in which no mixing takes place, the water returns to the heater from which it emerges at the same temperature as before ready to commence another cycle round the system.

It can easily be seen that, in passing through the exchanger, the stream of hot water gives heat to the cold stream, raising its temperature and thereby being cooled itself. Consequently the heat lost by the hot stream in any time is equal to that gained by the cold stream in the same time together with the heat lost by cooling. This cooling correction is reduced to a very small value by a suitable arrangement of the circulating pipes inside the exchanger, and a rough determination of it is sufficient. The temperatures of the hot and cold streams on entering and leaving the exchanger are measured to $\frac{1}{10000}^{\circ}\text{C.}$ by platinum resistance thermometers and the respective rise and fall remain constant over variations of the rate of flow of the water of 20 x. If m grm is the mass of water flowing past any point in the circulating system in 1 second and s_1 and s_3 are the specific heats of water at $\left(\frac{\theta_1 + \theta_2}{2}\right)^{\circ}\text{C.}$ and $\left(\frac{\theta_3 + \theta_4}{2}\right)^{\circ}\text{C.}$ respectively, we have

$$m \cdot (\theta_4 - \theta_3) s_3 = m(\theta_2 - \theta_1) \cdot s_1 + h,$$

where h is the heat lost by cooling. Hence we can find the ratio of s_1 to s_3 . If we adopt the 15°C calorie, the specific heat of water at 15°C is 1, and it is obvious that its value at any other temperature can be found from this experiment, for the mean temperature of the hot and cold streams in passing through the exchanger can be brought to any value by suitably adjusting the temperatures of the heater and cooler respectively.

The result of this experiment can be summed up by saying that it confirms the values obtained with Callendar and Barnes' continuous flow electrical method. These results are accordingly regarded as the most accurate values of the specific heat of water which have so far been obtained.

88. The Choice of a Thermal Unit—We are now in a position to discuss the various definitions of the calorie which have been suggested as a result of these experiments revealing a variation of the specific heat of water with temperature. We shall consider only three of the many suggestions which have been made

(a) The **15° C. calorie**. This has already been defined (Art 86), and was chosen because it is a temperature at which the mechanical equivalent of heat is known with great accuracy, a paramount consideration in the choice, and because it is a temperature to which other physical quantities have been referred

(b) The **mean calorie**, which is $\frac{1}{100}$ of the amount of heat required to raise 1 grm of water from 0° C to 100° C. While this is of use in certain cases, its great objection is that it is so difficult to correlate it with other definitions of the calorie

(c) Callendar has suggested that the calorie should be defined as $\frac{1}{10}$ of the amount of heat required to raise 1 grm of water from 15° C to 25° C. He supports this definition on the grounds that a finite range of temperature is used in all experiments on calorimetry, that the range chosen is quite easily attainable, and that the value of this calorie is very nearly equal to the mean calorie.

No universally accepted decision has yet been made from these suggestions, although the first two seem to be the most commonly used. So for the present it is still necessary to specify the particular calorie which is being used in really accurate measurements involving quantity of heat

89. The First Law of Thermodynamics.—The result of Joule's experiments may be conveniently summarised under the First Law of Thermodynamics, which states that when a given amount of work is done an equivalent amount of heat is produced, and when a certain quantity of heat disappears an equivalent amount of work is always obtained

It is clear that this amounts to saying that, besides kinetic and potential energy, there is yet another form called heat, and that the conservation of energy is still true when taken to include this new form. The First Law of Thermodynamics, in fact, is merely a particular case of the Conservation of Energy. We have already had one example of its application in the case of Mayer's calculation of J from the difference of the specific heats of a gas. The heat absorbed by a gas at constant pressure is used in two different ways; some of it is used to raise the temperature of the gas, that is, to increase its internal energy, while the

rest goes to supply the work done by the gas in expanding against the external pressure, that is, it re-appears as energy external to the gas. This case exemplifies the principle which is true of all such changes, for when a system absorbs heat, it is, in general, used up partly to increase the internal energy and partly to do external work. In fact, if a system absorbs a quantity of heat dQ , which produces an increase dU in its internal energy and causes it to do amount of external work dW , then

$$dQ = dU + dW \quad . \quad . \quad . \quad (44)$$

This equation is the mathematical expression of the First Law of Thermodynamics.

EXAMPLES ON CHAPTER VIII

1 Discuss the caloric theory of heat, and give a critical survey of the evidence which led to its downfall and substitution by the view that heat is a form of energy

2 Discuss the evidence for our belief that heat is a form of energy (*O and C*)

3 Enumerate some of the more important methods of experiment used to determine the mechanical equivalent of heat. Assuming that in one of Count Rumford's experiments the work of one horse could heat 26.6 lb of water 180°F in $2\frac{1}{2}$ hours, compare the performance of this horse with the standard Horse Power (772 ft-lb of work are required to raise the temperature of 1 lb of water 1°F) (*Camb Schol*)

4 Give a short account of Joule's work on the Conservation of Energy, and especially the ground of the objections which were raised to his view that when mechanical work is done by a thermal engine heat disappears (*Camb Schol*)

5 Give a critical account of the methods available for determining the mechanical equivalent of heat

In the absence of bearing friction a winding engine could raise a cage weighing 1000 kg at 10 metres per sec, but this is reduced by friction to 9 metres per sec. How much oil initially at 20°C is required per sec to keep the temperature of the bearings down to 70°C ? (Sp ht of oil = 0.5, $g = 981$ cm per sec per sec, $J = 4.2 \times 10^7$ ergs per calorie) (*O and C*)

6 Give a detailed account of Rowland's experiments on the mechanical equivalent of heat, pointing out how he improved on Joule's previous experiments. What light did his results throw on the problem of the variation of the specific heat of water with temperature?

7 Define specific heat, and explain why the specific heat of a gas at constant pressure is greater than that at constant volume? Obtain an expression for the difference between the two values.

How may one of these specific heats be determined experimentally? (*O* and *C*)

8 How is the specific heat of a gas at constant volume measured?

Calculate a value for the difference of the specific heats of hydrogen at constant pressure and constant volume, given that 1 grm of hydrogen occupies a volume of 11.2 litres at normal temperature and pressure, and that the mechanical equivalent of heat is 4.2×10^7 ergs per calorie (*Camb Schol*)

9 What is meant by (a) the specific heat of a gas at constant volume, (b) the specific heat of a gas at constant pressure, (c) the statement that the specific heat of saturated steam is negative?

Calculate a value for the mechanical equivalent of heat, given that the specific heat of oxygen at constant volume is 0.115 and at constant pressure 0.217, and that the mass of 1 litre of oxygen at normal temperature and pressure is 1.433 grm. Point out any assumptions made in the calculations (*Camb Schol*)

10 Describe the continuous flow method of determining the mechanical equivalent of heat. Discuss the advantages of this method (*Camb Schol*)

11 Discuss Callendar and Barnes' continuous flow method of measuring the mechanical equivalent of heat.

In an experiment using this method, the P.D. across the wire was 3 volts and the current 2 amps, the rise in temperature of the water 2.7°C and the rate of water flow 30 grm per minute. When the rate of flow was increased to 48 grm per minute, the P.D. to 3.75 volts and the current to 2.5 amps, the rise in temperature of the water is the same. Explain these results, and use them to calculate a value for the mechanical equivalent of heat (*Camb Schol*)

12 A bullet of mass 50 grm enters a block of wood with a velocity of 10,000 cm per sec. What is the heat developed in calories if the bullet is brought to rest in the wood?
 $1 \text{ calorie} = 4.2 \times 10^7 \text{ ergs}$

13 State the First Law of Thermodynamics

A rope brake on the flywheel of an engine carries a load of 200 lb at one end and 20 lb at the other and the diameter of the wheel is 4 ft. If the wheel is running at 200 r.p.m. find how much heat is being generated by friction at the brake per minute. Take 778 ft.-lb. as equivalent to one British thermal unit (*Camb Schol*)

14 Describe some method of measuring the mechanical equivalent of heat

If 778 ft.-lb. of work are required to raise the temperature of 1 lb. of water one degree Fahrenheit, what is the value of the mechanical equivalent of heat in C.G.S. units? $g = 32$ ft. per sec. per sec., 1 ft. = 30.46 cm (*Oxford Schol*)

15 Describe some simple method of determining the mechanical equivalent of heat

Calculate the difference of temperature between the water at the top and at the bottom of Niagara Falls, which are 50 metres high. The mechanical equivalent of heat is 4.2×10^7 ergs per calorie (*Oxford Schol*)

16 Explain briefly the simplest method you know of measuring the mechanical equivalent of heat

A motor-car weighing 2 tons is brought to rest by its well adjusted 4-wheel brakes from a speed of 90 miles an hour.

If the brake mechanism on each wheel weighs 16 lb., calculate the greatest possible rise in temperature. (Specific heat of brake material = 0.140, $J = 1400$ ft.-lb. per lb. °C) (*N.U.J.B.*)

17 Find an expression for the heat developed in a conductor when an electric current flows through it

Give an account of the work of Callendar and Barnes on the determination of the specific heat of water and its variation with temperature (*Tripes*, Part 1)

18 Describe some method which has been used to measure the specific heat of water at different temperatures

Give a sketch showing the kind of curve which represents the results of such experiments (*Camb Schol*)

19 Give a critical discussion of the evidence which has shown that the specific heat of water varies with temperature and state the conclusions which have been reached. How do the results affect the definition of the calorie?

CHAPTER IX

THE KINETIC THEORY OF GASES

90. The Structure of Matter.—We have seen in the last chapter how a long series of experiments culminating in the classic work of Joule led to the abandonment of the caloric theory of heat and its replacement by the view that heat is a form of energy. The question at once suggests itself, what sort of energy? As it resides in matter, we cannot attempt to answer this question until we have some conception as to the structure of matter. Historically the necessary amount of information was already available, having been obtained in the attempt to explain the laws of chemical combination.

There are only two possible hypotheses as to the structure of matter, either it is a continuous substance, capable of being subdivided indefinitely and filling the whole of the space which it occupies, or it consists of a collection of discrete minute particles separated from one another by distances of about the same order of magnitude as the size of the particles themselves. On this second view, a piece of matter does not fill up the whole of the space which it occupies, as there is a considerable amount of empty space between the particles. Nevertheless this space is evidently jealously guarded against intruders, for it is quite impossible to send any ordinary particle through a metal sheet without making a hole in it. Possibly the atoms prevent the entrance of the intruder by rapid motion in the same way that it is impossible to put one's finger through a rapidly revolving bicycle wheel. On the first view the smallest piece of a substance possesses all the properties with which a large piece is endowed, that is, not only the chemical properties but also such physical properties as hardness, expansion, and so on. It is at once evident that this view closes the door on any attempt to explain or correlate these physical and chemical properties in different substances. Substances differ in these respects because they are made of different "stuffs"; there is nothing more to be said about it. But on the discontinuous view of matter,

the small discrete particles composing a substance are supposed to be the smallest piece of the substance which can exist and retain the identity of the substance. They are called **molecules**; it is not asserted that they cannot be split up, but merely that, if they are subdivided, the separate parts will differ in identity from the original substance and possibly from one another. While the molecule is endowed with the chemical properties of the substance, it does not possess the properties of the substance in bulk, such as its hardness, expansion, and so on. These are due to the way in which the different molecules are arranged and held together to form a piece of the substance. It is easily seen that this view of matter has the initial virtue of leading to some *explanation* of its physical properties. It was quite possibly an intuition of this sort which led the early Greek philosophers Democritus, Leucippus, and Lucretius to put forward the atomic theory, the word atom in their theory having the same meaning as the molecule defined above.

There was more than intuition in it though. They explained compressibility as the pushing of the molecules of the substance closer together, the diffusion of gases through one another as the mixing of their molecules, and solution as the mixing of the molecules of the solute in between the spaces of those of the solvent. They saw that one substance was harder than another because its molecules attracted each other more strongly. But their theory failed to win any general assent, as so many others have done, because it was not based on quantitative laws; indeed its founders were unable to adduce any quantitative evidence in its favour. This forms yet another example of the importance of measuring things in numbers in scientific work.

91. The Atomic Theory.—The atomic theory was successfully revived by Dalton at the beginning of the nineteenth century to explain the fundamental gravimetric laws of chemical combination. How is it possible to explain that 1.008 grm of hydrogen always combine with 8 grm. of oxygen to form 9.008 grm of water, for example, on the continuous view of matter? The only thing which can be said is to assert that they are always found in that

proportion in water, which is obviously no explanation at all. But if we assert that an element consists of very small discrete particles, called atoms, which are the smallest part of the element which can exist and retain the identity of the element, and that the atoms of one element are identical with one another and different from those of any other element, the explanation of the above fact follows at once. An atom means literally that which cannot be cut, but we do not assert that it is impossible to split an atom, but merely that, if this is done, the parts obtained will differ in identity both from the original element and possibly from one another. *The atom is, in fact, the smallest part of an element which can take part in a chemical change.*

In the case of water quoted above, it is found that two atoms of hydrogen combine with one atom of oxygen to form what is evidently one molecule of water. The molecule is a company of atoms then. The atomic theory proved very successful in explaining the laws of chemical combination, and by enabling chemical reactions to be represented by the corresponding equation provided a stimulus to chemical research, the intensity of which it is hard to over-estimate. In spite of its great success in this field, there were some chemists, such as Ostwald, who refused to accept the theory on the grounds that it was not really essential and that there was no direct evidence for the existence of atoms. Their doubts were finally removed in 1908, when Rutherford succeeded in counting the number of atoms of helium shot out by a piece of radium in a given time.

Finally, Gay-Lussac's law of the combination of gaseous substances by volume was explained by Avogadro's hypothesis, which asserts that equal volumes of all gases measured at the same temperature and pressure contain equal numbers of molecules. This led to the discovery that hydrogen and many other gases are not composed of single atoms in the free state, but of molecules containing two or more atoms. *The molecule, then, may be defined as the smallest part of a substance which can exist in the free state.*

Nowadays, the mass of decisive physical evidence which has been collected in its favour has raised the atomic theory from the rank of a hypothesis to that of an established fact.

That matter does not fill the whole of the space which it occupies has been shown by projecting large numbers of electrons and atoms of helium through thin metal sheets without making any holes in them. Although atoms are too small to be seen even with the best microscope on account of their being so much smaller than the wave-length of visible radiation, they, or rather their effects, have been photographed by the much shorter X-rays, which has also led to the discovery of their arrangement in crystals and the measurement of their size and distance apart. It is found that atoms are of the order of 10^{-8} cm in diameter and are about the same distance apart in solids, a little further apart in liquids, and some ten times further apart still in gases at ordinary pressures.

92 The Kinetic Theory of Matter.—It is now evident that there are only two possible forms of energy which heat can assume, it must be either the potential or kinetic energy of the molecules. In certain cases it is perhaps partly in one form and partly in the other. Now it is well known that if the tap of an exhausted flask is opened the air rushes in and fills it in about 0.1 sec. This can only be explained by assuming that the molecules of the gas are in rapid motion, and so some of the heat in their case is in the form of kinetic energy of the molecules. Again, a solid expands when it is heated, that is, its molecules move further apart. The molecules must be attracting one another to account for the cohesion of the solid and so some work will have to be done to move them apart. Therefore some of the heat given to the solid to cause it to expand becomes potential energy of the molecules.

We shall now assume that these two principles are true in general and shall proceed on that basis to explain in a qualitative way the thermal properties of matter. Our theory, then, will be based on the following principles:

- (a) Matter consists of molecules
- (b) The molecules are in rapid motion
- (c) The molecules attract one another with a force which decreases as they get further apart

The first principle is to be regarded as definitely established by the evidence outlined above, but the other two are of a tentative nature, whose ultimate justification

depends on their success in explaining the experimental facts

We shall endeavour to explain the following facts :

- (a) The three states of matter
- (b) Expansion
- (c) Change of state
- (d) Conduction

The characteristic feature of a gas is that it has neither size nor shape. That is, it fills the whole of the space open to it, if that space is enlarged, it expands so as to fill uniformly the whole of the enlarged space presented to it. This is evidently due to the rapid motion of the molecules, combined with the fact that their attraction for one another has decreased to nothing on account of their large distance apart. The molecules spend most of their time moving about independently and therefore travelling in straight lines, and the only thing that restricts them is collisions with the walls of the containing vessel. Hence they will fill the whole of the space open to them. In a gas, then, we may say that the motion of the gas is the predominating factor, their attraction playing little or no part in determining its properties.

A liquid has size but no shape. Now the molecules of a liquid must be closer together than in a gas because of its smaller volume. For example, 1 c.c. of water produces about 1600 c.c. of steam, and so the molecules are about $\sqrt[3]{1600}$, or 12, times closer together in water than in steam. We should expect the attractions to make themselves felt in the case of a liquid then. They are evidently responsible for its definite size, for as soon as a molecule tries to get away from the body of the liquid in the attempt to fill the whole of a vessel, for example, it is prevented from escaping from the surface of the liquid by the attraction of the molecules below it. The mutual attraction of the molecules of a liquid ensure its definite size and by doing so cause its surface to behave like a stretched skin, which is the well-known phenomenon of surface tension. But a molecule in the body of the liquid does not feel any such attraction, because it is equally surrounded on all sides by molecules pulling it and so their attractions cancel one another out. Hence the molecule is quite free to move

about from one part of the liquid to another. In fact, the liquid has no shape, as the molecules are quite free to adjust themselves to that of any vessel which they may be occupying. In a liquid, then, the motion of the molecules and their attraction play an equal part in determining its properties.

A solid has both size and shape. The molecules are still closer together in this case than in a liquid and so their attraction is even greater. The attractions must be so great and of such a nature that each molecule is allotted a definite place from which it cannot depart. The only motion permitted to it is an oscillation about this position. This explains why a solid has a definite shape. It is now clear why a large crystal, the simplest sort of solid, can only be obtained if it is allowed to grow slowly. There is only one permissible arrangement for the molecules, and so the molecules of the solute have to be presented in the right way to the surface of existing crystal in order to be incorporated in it. Many of them will be presented in the wrong way as their motion around the crystal is purely random. So the crystal must be given time to reject these and to accept only those which are presented correctly. It is evident that a solid is formed under ordinary conditions by crystals growing simultaneously at a large number of points in the liquid. They cannot grow very far before reaching another crystal and so the resulting solid is a large number of very small crystals packed together in an irregular way. This has been shown to be the case by X-ray analysis, even for those solids which show no trace of crystalline structure under the microscope. We should add that the X-ray investigation of crystal structure has also shown that it is the atom and not the molecule which forms the unit of which the crystal is built up, for example, a crystal of rock-salt does not consist of molecules of sodium chloride arranged according to a certain pattern, but of atoms of sodium and atoms of chlorine arranged in a certain way. But this does not affect the general tenour of the above argument. In a solid, then, the mutual attraction of the atoms plays the predominating part in determining its properties.

When a solid is heated, more energy is given to its molecules, that is, they will oscillate more violently about their equilibrium position. So the molecules will move

further apart, that is, the solid expands. As more heat is supplied to the solid, a time will be reached when the molecules are so far apart that their attractions can no longer hold the upper hand and keep them in one fixed position, that is, the molecules become free to move about in the body of the substance, which has therefore changed to a liquid. As the molecules are further apart in the liquid than in the solid at the same temperature, heat must be supplied equivalent to the work done in pulling the molecules apart against their mutual attraction. This is the latent heat of fusion of the solid.

Let us suppose that we have a vertical column of gas, which is hotter at the top than the bottom. On our theory, this means that the molecules at the top are moving about more rapidly than those at the bottom. This increased energy of motion will be communicated to the bottom partly by collisions and partly by the actual translation of the molecules at the top to the bottom. In other words, heat will be conducted by the gas from the place where it is hot to the place where it is cold, and the flow of heat will obviously continue until the difference in temperature has been destroyed. A similar explanation applies to the conduction of heat by solids which are good conductors, the carriers being the free electrons which are also responsible for the conduction of electricity. To sum up, this theory, known as the kinetic theory of matter, has succeeded in explaining in a general way the fundamental thermal properties of matter. It has not been necessary to make any *ad hoc* assumptions, and so the conceptions of the motion of the molecules and their mutual attraction, on which the explanation was based, are sufficiently verified to warrant an attack on facts of a more definite nature. Before doing this it may be as well to illustrate the meaning of an *ad hoc* assumption by a concrete example. Expansion and the conduction of heat were explained on the caloric theory by assuming that caloric is a self-repellent fluid. This may not unfairly be called an *ad hoc* assumption, since it is made merely for the purpose of explaining the above two facts. This should be contrasted with the way in which the same two facts were explained on the kinetic theory, the explanation following quite naturally from the two general

principles of the theory These two principles may be called *ad hoc* assumptions, for they were definitely formulated to explain certain experimental facts, but there is no objection to this, as every theory must start with certain assumptions, which should be based on experimental fact The objection arises when it is necessary to make a new assumption to explain every new fact When that state of affairs is reached it is time to abandon the theory and seek for a fresh one It was precisely a situation of this sort which led to the abandonment of attempts to explain why it is impossible to detect the motion of the earth through the ether and their replacement by the Theory of Relativity

93. The Pressure of a Gas.—Let us consider a cylinder containing a fixed mass of gas enclosed by a piston On the kinetic theory the molecules are to be regarded as moving about independently at high speed and colliding with the walls of the cylinder and the piston The molecules will move in straight lines except when they come close enough for their mutual attraction to become sensible and cause a change in both the magnitude and direction of the velocity of the two molecules Such an occurrence will be called an **encounter**, and it is to be emphasised that it does not involve actual contact between the two molecules, if indeed such a statement has any real meaning There will be a continual stream of molecules striking the piston and rebounding from it, and they will produce a force on it just as a stream of sand particles produces sufficient force on a surface to clean paint off it It is the rebounding of the molecules of the gas from the piston which is responsible for the pressure of the gas If the volume of the cylinder is halved by pushing in the piston, the number of molecules rebounding from it in a given time will be doubled, and so the pressure will be doubled also This is Boyle's law If the volume of the gas is kept the same while its temperature is increased, both the number of impacts on the piston in a given time and the force due to each impact increases, since the molecules are now moving more rapidly; therefore the pressure of a gas at constant volume increases with rise of temperature So the kinetic theory of matter is able to give a qualitative explanation of the thermal properties of a gas

94. Evaporation.—It may be as well to summarise the experimental facts concerning evaporation, which have been described in Chapter VII, before attempting to explain them on the kinetic theory

(a) If a small quantity of liquid is introduced into a vacuum, it immediately evaporates to an unsaturated vapour, which obeys Boyle's law roughly

(b) If further quantities of liquid are introduced, a time is reached when no further evaporation occurs. The vapour is now said to be saturated, for its pressure is a maximum for that given temperature, and is quite independent of its volume

(c) Saturation vapour pressure increases with rise of temperature

We have seen that the molecules are moving about quite freely in the body of a liquid, but that as soon as they try to escape from the surface they are prevented from doing so by the attraction of the other molecules. Now we shall see later that, at a given temperature, the molecules are not all moving at the same speed. It is the average speed that is fixed when the temperature is specified, most of the molecules will be moving at or near to this speed, but some will be moving more slowly and others more quickly. There will always be some molecules, then, near the surface and moving towards it, which are endowed with sufficient speed to enable them to overcome the attractions of the other molecules, so they will escape. They will then move about independently colliding now and again with the walls of the exhausted vessel into which the liquid has been introduced. In fact, the molecules which have escaped from the liquid form a gas. This process of escape may continue until all the liquid has disappeared. The gas which is thus produced will obey Boyle's law for the reasons outlined in the previous article.

Let us suppose that further quantities of liquid are introduced into the vacuum, producing still more vapour in the space above the liquid. At the stage when some liquid is still left, two things are happening. Firstly, there is a certain number of molecules escaping in every second from the liquid, a number which will be controlled entirely by the temperature of the liquid. Secondly, there will be a

certain number of molecules returning to the liquid in every second due merely to the fact that, in their path in the space above the liquid, collisions with the walls of the vessel and encounters with other molecules will occur, the ultimate result of which will be to direct the molecule towards the surface of the liquid once more. If it reaches the surface before its velocity is changed in direction by another encounter, it will be captured by the liquid. The number of molecules returning to the liquid in this way is controlled by the number in unit volume of the vapour. Therefore, when sufficient vapour has been produced by evaporation to make the number of molecules returning to the liquid per second equal to the number leaving in the same time, no further evaporation takes place, in fact, the vapour is saturated. It is exerting the biggest pressure it can at the given temperature, because its density is a maximum. We can see this in another way. The number of molecules entering unit area of the surface of the liquid in unit time is equal to the number striking unit area of the walls in the same time, since the motion of the molecules is quite random as regards direction. At saturation, when the number entering the surface is greatest, the number of molecules striking unit area of the walls in unit time, and therefore the pressure of the vapour, is also a maximum. The pressure is independent of the volume, because, if we attempt to increase it by decreasing the volume of the vapour, we increase the number of molecules of vapour in unit volume and therefore the number returning to the liquid in unit time. But no change is produced in the number of molecules leaving the liquid in the same time, and therefore the number returning to the liquid is greater than that leaving it, that is, condensation sets in. It continues until the two opposing streams are equal once more, that is, until the vapour pressure has resumed its original value. It is easy to see that an attempt to decrease the pressure of the vapour by increasing its volume merely results in further evaporation until the pressure has increased to its saturation value once more. It should be noticed that the equilibrium between a liquid and its saturated vapour is not static, as it appears to be.

the same molecules do not invariably remain in the

liquid, for there is a constant interchange going on between it and the vapour. The appearance of rest is produced by the balancing of the opposing streams of molecules, and so the liquid and vapour are said to be in **dynamic equilibrium**. The same state of affairs occurs in reversible chemical reactions, and will be met with later on in this book in connection with radiation (Art 161). In the same way, evaporation is not the change from liquid to vapour only, but is due to the rate of escape of the molecules exceeding their rate of return, the converse condition obtaining during condensation.

If the temperature of the liquid is raised, the average velocity of the molecules is increased, and so a greater fraction will have sufficient energy to enable them to escape from the surface of the liquid. Therefore the number of molecules escaping from the liquid in every second will increase and upset the equilibrium between the opposing streams. Hence evaporation will set in and continue until the density and therefore the pressure of the vapour has increased to such an extent, that the number of molecules returning to the liquid in every second is equal to the number escaping once more. Thus saturation is again established with a greater vapour pressure than before. That is, the saturation vapour pressure of a liquid increases with rise of temperature. We can also see that the same results will be obtained if the liquid is in the presence of air or any other gas, but that a longer time will be required to establish equilibrium on account of the encounters between the molecules of the vapour and those of the foreign gas. This prediction is borne out by experiment.

We have seen that evaporation entails the escape, from the liquid, of those molecules whose speed is above the average and therefore it decreases the average velocity of those left behind. In other words, evaporation is accompanied by cooling, a fact that has been noticed in Chapter VI.

We may sum up the present position by saying that the kinetic theory has been able to offer a satisfactory qualitative explanation of the existence of the three states of matter, their expansion on being heated, the change from one state to the other and of the conduction of heat by matter. It has also been able to account for the pressure

of a gas and the laws which that pressure obeys in a general way, and has given a complete explanation of the facts concerning evaporation and vapours. The time has now arrived, in view of this success, to subject the theory to the more severe test of explaining some of the quantitative laws of heat. We shall be wise to attempt the simplest ones first and so we shall endeavour to derive the ideal gas equation from the kinetic theory. This is the simplest law we can choose because it is obeyed approximately by all gases and is the limit to which they all tend at infinitely low pressure. This is not the case with solids and liquids, in which the coefficient of expansion, latent heat, etc., varies from one substance to another.

95. The Model of an Ideal Gas.—An ideal gas obeys the following laws :

(a) Its pressure, volume, and temperature are related by the ideal gas equation

$$pv = RT. \quad . \quad . \quad . \quad (45)$$

(b) If several different gases are occupying the same vessel, the total pressure exerted by all the gases is equal to the sum of the pressures which each gas would exert if it occupied the space alone. This is Dalton's law of partial pressures and is true, of course, only if the different gases do not react with one another chemically.

(c) Equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules. This is Avogadro's hypothesis, and was suggested as an explanation of Gay-Lussac's law of the combination of gases by volume.

Our task is to construct a model, based on the kinetic theory, which will obey these laws. We shall make the following assumptions in the course of our investigation :

(a) The molecules are of negligible size and do not attract one another. This is justifiable because we are trying to construct a model which represents the behaviour common to all gases and so it must not include any factors which may vary from one gas to another. Size of molecule and inter-molecular attraction are the only two such factors and so they are neglected. Incidentally this shows why the behaviour of all gases tends to become the same at

infinitely low pressures, since it is under these conditions that the properties peculiar to each gas become of no effect, since the molecules are so far apart compared to their size

(b) The time spent in encounters is negligible compared with that during which the molecules are moving independently. This assumption is justified for the same reason as the previous one

(c) The encounters between one molecule and another or one of the containing vessel are perfectly elastic. This is evidently the case for encounters between molecules of the gas and must be true on the average for those between a molecule of the gas and the wall of the containing vessel, although it may not be true for individual encounters. For, if it were not true on the average, it would mean that the gas was either losing or gaining energy at the expense of the containing vessel, which is contrary to experience.

96. An Expression for the Pressure of an Ideal Gas.—

Let us suppose that a given mass of gas is contained in a cube of unit side and that the co-ordinate axes Ox , Oy , Oz are parallel to the three sides of the cube. Let the molecules be divided into r groups, the first group consisting of n_1 molecules whose velocity is c_1 with components u_1 , v_1 , w_1 parallel to Ox , Oy , Oz respectively, the second group consisting of n_2 molecules whose velocity is c_2 with components u_2 , v_2 , w_2 and so on. When a molecule of the first group rebounds from the face A of the cube perpendicular to Ox , it suffers a change of momentum $2mu_1$, where m = the mass of a molecule, since the encounters are perfectly elastic. The number of impacts made in unit time by the molecule on the face A is $\frac{u_1}{2}$, since the time spent in encounters is

negligible compared to that when the molecule is moving independently and so its velocity parallel to Ox may be regarded as constant and equal to u_1 . Hence the total change of momentum suffered in unit time by all the molecules in the first group due to rebounding from the face

$$\begin{aligned} A &= n_1 \cdot 2mu_1 \cdot \frac{u_1}{2} \\ &= n_1 mu_1^2. \end{aligned}$$

But, by Newton's Second Law of Motion, force is equal to change of momentum in unit time, and so this is the force of the face A on the first group of molecules and therefore the force of the first group of molecules on the face A.

∴ the total force of the gas on the face A

$$\begin{aligned} &= n_1 m u_1^2 + n_2 m u_2^2 + \dots + n_r m u_r^2 \\ &= m(n_1 u_1^2 + n_2 u_2^2 + \dots + n_r u_r^2) \\ &= m n \bar{u^2} \end{aligned}$$

where
$$\bar{u^2} = \frac{n_1 u_1^2 + n_2 u_2^2 + \dots + n_r u_r^2}{n_1 + n_2 + \dots + n_r}$$

and
$$n = n_1 + n_2 + \dots + n_r,$$

and $\bar{u^2}$ is the number of molecules in unit volume of the gas

$\bar{u^2}$ is the mean of the squares of the components of the velocities parallel to O*x*

Since the face A is of unit area, the force on it is equal to the pressure of the gas, p

$$\therefore p = m n \bar{u^2}$$

Similarly, the pressure on the other two faces is given by

$$\begin{aligned} p &= m n \bar{v^2}, \\ p &= m n \bar{w^2} \end{aligned}$$

These pressures are known to be equal by experiment and this is verified by our theory, since $\bar{u^2} = \bar{v^2} = \bar{w^2}$ if there is no motion of the gas as a whole in any one direction

Adding these three expressions for the pressure, we have

$$\begin{aligned} p &= \frac{1}{3} m n (\bar{u^2} + \bar{v^2} + \bar{w^2}), \\ \therefore p &= \frac{1}{3} m n C^2, \end{aligned} \quad (46)$$

where
$$C^2 = \frac{n_1 u_1^2 + n_2 u_2^2 + \dots + n_r u_r^2}{n_1 + n_2 + \dots + n_r}$$

C is called the **root mean square velocity** of the molecules; it is the square root of the average of the squares of the velocities. It is of interest to notice that it is *not* equal to the average velocity. For the average of two velocities 8 and 10 is 9, but their root mean square is

$$\sqrt{\frac{64 + 100}{2}} = \sqrt{82} = 9.06.$$

We can re-write equation (46) in the form

$$p = \frac{2}{3} m n C^2$$

This shows us that the pressure of an ideal gas is equal to two-thirds of the total kinetic energy of the molecules contained in unit volume of the gas

97. The Distribution of Velocities among the Molecules.—In deriving an expression for the pressure of an ideal gas, we have tacitly made two assumptions. Firstly, we have taken it for granted that the number of molecules n_1 moving with a given velocity c_1 always remains the same, secondly, we have completely ignored the changes in velocity of a molecule due to its encounters with others, for we have treated each one as if it moved for the whole time with its velocity unchanged except by encounters with the faces of the cube. Can we justify such sweeping assertions? There can be no doubt that the velocity of any individual molecule is continually changing due to its encounters with others, but these changes are subject to the condition that the total kinetic energy of all the molecules in the cube is constant. For this is the amount of heat in the gas, which remains the same at the same temperature. Therefore the average kinetic energy of the molecules is always the same at the same temperature. The word *average* gives the key to the solution of our difficulties. It is evidently hopeless to attempt to follow the path of an individual molecule, so we must turn to the statistical method, in which we consider the number of molecules moving with a given velocity. We should really say the number whose velocity lies between certain limits, but if we suppose that we are only measuring the velocity to the nearest whole number, the number moving with a velocity of 300 yards per second means the number whose velocities lie between 299.5 and 300.5 yards per second. Maxwell succeeded in showing that in a gas at constant temperature, whatever the distribution initially, the gas would quickly reach a steady state in which the number of molecules moving with a given velocity is constant. This does not mean that it is always the same molecules which are moving with a given velocity, but that if dn_1 molecules change their velocity in a time dt from c_1 to some other value, then dn_1 molecules change their velocity to c_1 from some other value in the same time. This is true, not only for the whole unit cube of gas, but for any small element

of volume provided that it contains a very large number of molecules. So we see that our first assumption is justified, and the same law also leads to the justification of the second. Suppose we consider a molecule starting from the face A of the cube with the x -component of its velocity equal to u_1 . After a very short time its velocity will change owing to an encounter with another molecule. But since Maxwell's law is true even for a small volume of the gas, its place will at once be taken by another molecule in the same element of volume. To put it in another way, our first molecule has *left* the class of molecules with x -component of velocity equal to u_1 . But since the gas is in a steady state, its place is immediately taken by another molecule which *enters* the class of molecules with x -component of velocity equal to u_1 from some other class. This second molecule soon changes its velocity, but its place is at once taken by another molecule in the same element of volume and so on all the way across from one face of the cube to the other. In fact, the effect is just the same as if the original molecule had continued to move with its initial velocity, which is just what we have assumed.

We shall not give the result which Maxwell obtained for the distribution of the velocities among the molecules, as it is unnecessary for the calculations which we shall make. But it is most important to realise that Maxwell's law of distribution of velocities among the molecules follows merely from the application of the principles of classical mechanics to a system consisting of a very large number of particles exchanging energy by some sort of encounter. This branch of mechanics is called statistical mechanics. Maxwell's result and any other theorem in statistical mechanics applies so long as the system contains a very large number of particles exchanging energy by some sort of encounter, the nature of the particles themselves being immaterial.

98. The Ideal Gas Equation.—Now mn = the mass of unit volume of the gas, that is, its density ρ . So equation (46) may be re-written

$$\begin{aligned} p &= \frac{1}{3} \rho C^2, & . & . & . & . & (47) \\ \therefore \frac{p}{\rho} &= \frac{1}{3} C^2. \end{aligned}$$

But if the temperature is constant, the heat energy of the given mass of gas and so the total kinetic energy of its molecules is constant. That is, the mean square velocity, C^2 , is constant

$$\therefore \frac{p}{\rho} = \text{constant, if the temperature is constant,}$$

which is Boyle's law

If M = the molecular weight of the gas,
and V = the volume occupied by a gram-molecule of the gas,

$$\rho = \frac{M}{V},$$

$$\therefore pV = \frac{1}{3}MC^2 \quad . \quad . \quad . \quad (48)$$

Let us compare this equation with the ideal gas equation, which we will re-write for the sake of convenience,

$$pV = RT, \quad . \quad . \quad . \quad (45)$$

R being the gas constant for 1 gram-molecule of the gas
We see that our model will represent the behaviour of an ideal gas completely, provided that

$$\begin{aligned} \frac{1}{3}MC^2 &= RT, \\ \frac{1}{2}MC^2 &= \frac{3}{2}RT \quad . \quad . \quad . \quad (49) \end{aligned}$$

Dividing both sides by N , the number of actual molecules in 1 gram-molecule of the gas, called **Avogadro's number**, we have

$$\frac{1}{2} \frac{M}{N} C^2 = \frac{3}{2} \frac{R}{N} T.$$

But

$$\begin{aligned} \frac{M}{N} &= m, \\ \therefore \frac{1}{2} m C^2 &= \frac{3}{2} k T, \quad . \quad . \quad . \quad (49a) \end{aligned}$$

where $k = \frac{R}{N}$, and is called **Boltzmann's constant**. So we have succeeded in constructing a model of a gas which obeys Boyle's law and will also obey Charles' law and the law of the increase in pressure at constant volume, provided that the average kinetic energy of the molecules of the gas is proportional to its absolute temperature This is

in itself very satisfactory, but it is necessary to find further experimental support for this kinetic interpretation of temperature expressed by equation (49a)

99. The Kinetic Interpretation of Temperature.—The same method of statistical mechanics, which enabled Maxwell to find the distribution of velocities among the molecules of a single gas, can be applied to a mixture of gases. It should be emphasised at the outset that the problem is purely one of dynamics, and that the results are true for a system consisting of any kind of particles, large or small, provided that there are sufficient of them and that they are exchanging energy by some kind of encounter. In fact, the results have been applied to a system consisting of free electrons and also to the galactic system of stars. It is found that the steady state is reached when the average kinetic energy of the different sets of molecules is the same. If m_1 , C_1 , m_2 , C_2 , and so on are the mass and root mean square velocity respectively of the different molecules, then

$$\frac{1}{2}m_1C_1^2 = \frac{1}{2}m_2C_2^2 = \frac{1}{2}m_3C_3^2, \text{ etc.} \quad (50)$$

in the steady state

Therefore if a number of gases, the average kinetic energy of whose molecules is the same, is mixed, they will do so without exchange of energy on the whole. **On our view of heat, this means that they mix without exchange of heat and therefore they were at the same temperature before mixing.** But this is precisely the result we obtain from equation (49a), and so our kinetic interpretation of temperature is justified. We can now write

$$\frac{1}{2}m_1C_1^2 = \frac{1}{2}m_2C_2^2 = \frac{1}{2}m_3C_3^2 = \frac{3}{2}kT,$$

thus showing that k is a universal constant

100. Dalton's Law of Partial Pressures.—If we work out the pressure of a mixture of gases in equilibrium, we obtain the following result.

$$p = \frac{1}{3}s_1m_1C_1^2 + \frac{1}{3}s_2m_2C_2^2 + \frac{1}{3}s_3m_3C_3^2 + \dots;$$

where s_1 , s_2 , s_3 , are the number of molecules of the first, second, and third gas respectively in unit volume of the mixture.

But $p_1 = \frac{1}{3}m_1s_1C_1^2$ is the pressure which the first gas would exert if it occupied the space to the exclusion of the others, and is called the partial pressure of the gas. If p_2, p_3 are the partial pressures of the second and third gas, we have

$$p = p_1 + p_2 + p_3 + \dots,$$

which is Dalton's law of partial pressures.

101. Avogadro's Hypothesis.—Let m_1, s_1 , and C_1 be the mass, the number in unit volume, and the root mean square velocity of the molecules of one gas, and let the same letters with a subscript 2 represent the corresponding quantities for another gas. If their pressures are the same, from equation (46)

$$m_1s_1C_1^2 = m_2s_2C_2^2$$

If their temperatures are the same, from equation (50)

$$m_1C_1^2 = m_2C_2^2.$$

From these two equations, we have

$$s_1 = s_2$$

which is Avogadro's hypothesis

102. Graham's Law of Diffusion.—The rate at which a gas diffuses through a porous pot or into another gas will be determined by the average velocity of its molecules. It will be remembered that this is not equal to the root mean square velocity, but it can be shown that it is proportional to it. From equation (47), we have

$$C = \sqrt{\frac{3p}{\rho}},$$

$$\therefore C \propto \frac{1}{\sqrt{\rho}}.$$

That is, the rate of diffusion of a gas is inversely proportional to the square root of its density, which is Graham's law of diffusion

We have succeeded in constructing a model of an ideal gas which obeys the ideal gas equation, Dalton's law of partial pressures, Avogadro's hypothesis, and Graham's law of diffusion. Incidentally our investigation has led to an important interpretation of temperature. It shows

that the temperature of a body is measured by the average kinetic energy of its molecules. It should be emphasised that temperature is essentially a statistical quantity, it is meaningless to talk of the temperature of a system consisting of only a few particles.

103. The Calculation of Molecular Velocities.—It is a simple matter to calculate the root mean square velocity of the molecules of a gas at a given temperature and pressure from equation (47). This was first done by Joule in 1848, although Daniel Bernouilli had shown as far back as 1738 that the kinetic theory could account for the pressure and expansive force of gases. We shall take the case of hydrogen at N.T.P. as an example and use equation (49) as it illustrates more clearly the influence of temperature on the velocity. The gas constant R for 1 gram-molecule of the gas is a universal constant, whose value has been calculated in Art. 48 and is equal to 8.31×10^7 ergs per gram-molecule per $^{\circ}\text{C}$. Hence at 0°C . or 273°A , we have

$$\begin{aligned}\frac{1}{2} MC^2 &= \frac{3}{2} \times 8.31 \times 10^7 \times 273 \\ &= 3.403 \times 10^{10} \text{ ergs}\end{aligned}$$

This is the kinetic energy of a gram-molecule of any gas at 0°C . The root mean square velocity of the molecules of hydrogen at this temperature is given by

$$\begin{aligned}\frac{1}{2} \times 2.016 \times C^2 &= 3.403 \times 10^{10}, \\ \therefore C &= 1.84 \times 10^5 \text{ cm per sec.}\end{aligned}$$

The values at other temperatures or for other gases are obtained by substituting the appropriate value of the temperature and molecular weight. A few typical values are given in Table IX, in which special mention may be made of the case of the interior of a star. Even here the velocity is only of the same order as that of the stars themselves, and is still very small compared to that of cathode rays or α -particles. *It should also be noticed that the velocity of the molecules of air and hydrogen is of the same order as the velocity of sound in those gases at the same temperature.* We now see that the reason why the velocity of sound in a gas increases with temperature is because the velocity of its molecules increases. Sound is a disturb-

ance which is handed on, as it were, from molecule to molecule and so the rate at which it travels cannot exceed the speed of the molecules themselves. We may conclude by pointing out that these velocities have all been calculated without knowing the actual number of molecules in a given volume of the gas, this is an interesting example of how atomic constants can be calculated from purely macroscopic measurements.

TABLE IX

Substance	Molecular Weight, gm	Temperature in °C	Root Mean Square Velocity, cm per sec
Hydrogen . .	2.016	0°	1.84×10^5
Oxygen . .	32	0°	4.62×10^4
Carbon dioxide .	44	0°	3.94×10^4
Mercury vapour .	200	0°	1.85×10^4
Helium . .	4	0°	1.307×10^5
Matter in the interior of a star .	2	40,000,000°	7.06×10^7 or 440 miles per sec

104. Direct Evidence in Favour of the Kinetic Theory.—The kinetic theory of matter is supported by a considerable body of experimental facts of a qualitative nature in its application to solids and liquids and in the case of gases it has been advanced a stage further and has succeeded in explaining the quantitative laws of the ideal gas. Nevertheless, all this evidence is of a circumstantial nature and it is desirable to obtain direct evidence of the motion of thermal agitation of the molecules if at all possible. This term is a particularly appropriate description of the motion of the molecules due to their heat, a motion so rapid, so irregular, and yet leaving the gas as a whole motionless. As a matter of fact, one piece of evidence was already in existence, but its bearing on the kinetic theory had not been realised because the facts had been wrongly interpreted. We refer to the **Brownian movement**, discovered by a botanist, Robert Brown, in 1827.

He scattered some fine particles of pollen into a few drops of water, in which they remained suspended, and on observing them in the microscope he noticed that they were describing small irregular motions. He also noted that these movements continued indefinitely and never showed any signs of stopping or even abating. They are referred to as the Brownian movement and were attributed at first to surface tension, irregularities in the temperature of the water, vibrations, chemical action, and so on. All these explanations broke down, and the phenomenon remained unexplained until it was realised that it was due to the motion of thermal agitation of the molecules of the liquid. The irregularity of the motion of the particles points unmistakably to a similar irregularity in those of the molecules. The effect can only be obtained with very small particles for two reasons, firstly, the kinetic energy of the molecules is so small that they cannot communicate a finite velocity to a large particle. The second reason is rather more difficult to follow. It will be remembered that Maxwell showed that the velocities were distributed among the molecules according to a definite law and that this distribution was true for any small element of volume in the substance. Therefore if the particle is large, the force due to the impacts of the molecules on one side will be just counterbalanced by that due to those on the other and the nett force on the particle will be zero. But if the particle is so small that it suffers encounters with only a few hundred of the molecules of the liquid at any one time, the irregularities in the motion of the molecules will begin to manifest themselves. At one moment, it will be the molecules coming from the north which will have the greater momentum and so the particle will move southwards, then it will be those coming from the south-east which will predominate and drive the particle north-west and so on. Lastly the smaller the particle, the larger, the more irregular the movements will be, as is observed experimentally. That these movements are due to the motion of thermal agitation of the molecules has been recently been placed beyond all doubt by the determination of Avogadro's number from them, the value obtained agreeing very well with that obtained by entirely different methods.

105. The Viscosity and Thermal Conductivity of Gases.—Let us suppose that D, E, and F are three parallel and equidistant planes in a gas which is flowing from left to right (Fig 64). If the rate of flow decreases as we go from D through E to F, it is found experimentally that the gas sets up a force opposing this *relative motion of adjacent layers*. The property by virtue of which it does this is called its **viscosity**.

The following analogy will help us to understand its explanation on the kinetic theory. Consider the motion of a swarm of flies on a summer evening. We can distinguish two motions, the first, comparatively slow, of the swarm as a whole; the second, more rapid, of the individual flies moving in different directions and at different speeds within the swarm. A flow of gas is precisely similar to the motion of a swarm of flies. There is first of all the

motion of the gas as a whole, its velocity of drift, a motion shared equally by all the molecules, and then there is the much faster motion of thermal agitation of the individual molecules within the space occupied by the gas. In the type of motion

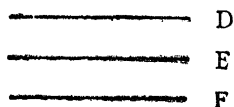


FIG 64

under consideration the velocity of drift is the same for all molecules in the same plane of the gas. Let us suppose that the distance between the planes D, E, and F is equal to the mean free path of the molecules of the gas, which means the average distance which they travel between two encounters. Some of the molecules of the gas in the plane D will be moving towards E on account of their velocity of thermal agitation, and on the average they will reach it without suffering an encounter on the way. So they will become part of the gas below E and yet have the velocity of drift appropriate to the plane D. In the same way some of the molecules from the plane F will pass through the plane E and become part of the gas above E but possessing a velocity of drift corresponding to the plane F. Therefore the velocity of thermal agitation causes a mixing of the molecules which decreases the velocity of drift above E and increases it below, that is, it will tend to stop the relative motion of the adjacent layers of the gas. But this is just what is meant by the viscosity of the gas.

The thermal conductivity of a gas is explained in precisely the same way. Let us suppose that D, E, and F are now planes in the gas such that the temperature decreases as we go from D to F through E. The molecules will have the velocity of thermal agitation corresponding to the plane of the gas they are in, but molecules from D will be continually passing through E carrying the velocity of thermal agitation corresponding to D with them, because, on the average, they will suffer no encounter between D and E. Hence the average velocity of the molecules of the gas below E is continually increasing, while that above is continually decreasing owing to the upward flow of molecules from F. That is, the temperature of the gas below E is rising while that above is falling, which means that the gas is conducting heat from D to F. It should be emphasised that both of these effects are due to the continual mixing of the molecules due to the random nature of their heat motion.

Maxwell predicted from the kinetic theory that both the viscosity and thermal conductivity of a gas are independent of pressure. If the pressure of the gas is halved, there are only half as many carriers of velocity of flow, in the case of viscosity, but each can carry its burden twice as far, since the mean free path is doubled. So the rate of transference of the velocity of flow is unaltered, that is, the viscosity is independent of pressure. The same argument applies to thermal conductivity. Both of these predictions have been verified experimentally for pressures at which the mean free path is small compared to the size of the containing vessel.

106. The Atomicity of Gases.—In constructing a model of the ideal gas we made certain assumptions (Art. 95), one of which was that encounters between molecules of the gas are perfectly elastic. This means that the sum of the kinetic energy of translation of the two molecules is unaltered by the encounter. This assumption is valid in the case of monatomic gases, for the only form which the kinetic energy can assume is energy of translation of the molecule. Is it true for polyatomic gases, that is, those which contain two or more atoms in the molecule? It is likely in their case that the atoms in the molecule are vibrat-

ing with respect to one another and the whole molecule may be rotating about one or more axes. There will be both kinetic and potential energies associated with these motions, and we shall refer to this energy as the **internal energy** of the molecule. It is evident that there may be an exchange between the translational kinetic energy and the internal energy of the molecules at an encounter and so the former may not be conserved at each individual encounter. But it must be conserved on the average, since the results we have obtained on this assumption are true both for monatomic and polyatomic gases. In other words, considering a large number of encounters suffered by a given molecule, the amount of translational energy converted to internal energy is equal to the amount of translational energy received from internal energy, and so on the whole the translational energy is conserved. So our investigation of the pressure of an ideal gas is true whatever its atomicity may be.

We can obviously throw some light on the atomicity of a gas, then, if we can calculate the ratio of the total energy to the translational energy of its molecules. If unit mass of the gas is heated through a rise of temperature dT , the increase in total energy $= C_v \cdot dT$, where C_v is the specific heat at constant volume of the gas. From equation (49), the increase in translational energy $= \frac{2}{3}\gamma \cdot dT$, where γ is the gas constant for unit mass of the gas.

$$\therefore \frac{\text{Increase in total energy}}{\text{Increase in translational energy}} = \alpha = \frac{C_v \cdot dT}{\frac{2}{3}\gamma dT} = \frac{2}{3} \cdot \frac{C_v}{\gamma}.$$

From equation (43), $\gamma = C_p - C_v$, where C_p is the specific heat at constant pressure of the gas.

$$\begin{aligned} \therefore \alpha &= \frac{2}{3} \cdot \frac{C_v}{C_p - C_v} \\ &= \frac{2}{3} \cdot \frac{1}{\gamma - 1}, \quad \cdot \quad \cdot \quad \cdot \quad (51) \end{aligned}$$

where $\gamma = \frac{C_p}{C_v}$, the ratio of the specific heats of a gas.

The interpretation of this equation is very interesting. Several gases, such as mercury vapour and the rare gases,

are known, for which γ is 1.67 or $\frac{5}{3}$. Substituting this value in equation (51), we find

$$\alpha = \frac{2}{3} \frac{1}{\frac{5}{3} - 1} = \frac{2}{3} \frac{1}{\frac{2}{3}} = 1,$$

that is, the total energy is equal to the translational energy. This means either that the molecules possess no internal energy, or that it does not change with temperature. This suggests that the molecules are monatomic, which was already known to be the case with mercury vapour from chemical evidence. The difficult problem of finding the atomic weights of the rare gases was solved by this means. The ordinary methods cannot be used since the rare gases do not enter into chemical combination. But the above value of γ shows that they are monatomic and so their atomic weights are equal to their respective molecular weights, which are obtained from the corresponding vapour densities.

Hydrogen, oxygen, nitrogen, and many other gases which are known to be diatomic from chemical evidence have the value 1.41 or $\frac{7}{5}$ for the ratio of the specific heats. Substituting this value in equation (51), we have

$$\alpha = \frac{2}{3} \frac{1}{\frac{7}{5} - 1} = \frac{2}{3} \frac{1}{\frac{2}{5}} = \frac{5}{3}$$

This shows that the internal energy is two-thirds of the translational energy.

It is found experimentally that, the greater the atomicity of the gas, the nearer the value of γ approaches to 1, and so from equation (51) the greater α becomes. Therefore the more complex the molecule, the greater the internal energy becomes compared to the translational energy, which is just what we should expect. Hence we see that the determination of γ combined with the kinetic theory throws valuable light on the constitution of the molecules of a gas.

107. The Equipartition of Energy.—The results obtained in the previous article concerning the total and translational energy of the molecules of a gas can be interpreted in a very striking way by means of a theorem in statistical mechanics due to Boltzmann, called the theorem

of the equipartition of energy It applies only to systems consisting of a very large number of particles, although the nature of the particles themselves is a matter of indifference, and only to those motions whose energy can be changed by encounters of some sort It states that the average energy of each degree of freedom of the motion of the particles is the same and is equal to $\frac{1}{2}kT$, where T is the absolute temperature of the system The number of degrees of freedom of the particle means, roughly speaking, the number of different types of motion possible to it, or the number of different co-ordinates needed to specify its position For example, the translational motion of a particle can take place in any direction in space and so possesses three degrees of freedom, since it requires three co-ordinates to define the position of a particle in space Hence the average translational energy of any molecule, irrespective of its atomicity, is $\frac{3}{2} kT$, which agrees with equation (49a), which has been shown to be true for any type of molecule

The theorem interprets the equality of the total and translational energies of a monatomic gas as showing that the atoms are either not rotating at all or cannot exchange their energies of rotation by encounters The ratio $\frac{5}{3}$ in the case of diatomic gases indicates that the molecules are rotating with two degrees of freedom in addition to the translation common to all types of molecule Hence

$$\alpha = \frac{(3 \frac{1}{2}k \frac{dT}{dT} + 2 \frac{1}{2}k \frac{dT}{dT})N_1}{3 \frac{1}{2}k \frac{dT}{dT} N_1},$$

where N_1 = the number of molecules in unit mass of the gas.

$$\begin{aligned}\therefore \alpha &= \frac{(3 + 2) \frac{1}{2}N_1 k \cdot \frac{dT}{dT}}{3 \cdot \frac{1}{2}N_1 k \frac{dT}{dT}}, \\ \therefore \alpha &= \frac{5}{3}.\end{aligned}$$

In the days when the atom was regarded as a round hard ball, this was taken to mean that the molecules of diatomic gases consist of two atoms arranged in a sort of dumb-bell structure, the two degrees of freedom of rotation corresponding to rotation about two mutually perpendicular axes at right angles to the line joining the atoms It would

be unwise to pay much attention to this structure in view of the present state of knowledge of the structure of the atom. Similar interpretations have also been made in the case of the more complex molecules.

108. The Specific Heat of Gases and Solids.—We shall conclude this account of the kinetic theory with a calculation of the specific heat of gases and solids based on the theorem of the equipartition of energy. Considering in the first place any monatomic gas, we see, from the fact that the molecules possess only the three degrees of translational energy, that the energy U of 1 gram-molecule of the gas at an absolute temperature T is given by

$$U = \frac{3}{2} NkT \\ = \frac{3}{2} RT,$$

where N is Avogadro's number and R is the gas constant for 1 gram-molecule of the gas

$$\therefore M_v = \frac{dU}{dT} = \frac{3}{2} R,$$

where M_v = the molecular heat at constant volume of the gas, that is, the amount of heat needed to raise 1 gram-molecule through 1°C . Taking $R = 8.31 \times 10^7$ ergs per gram-molecule per $^\circ\text{C}$. for the ideal gas (Art 48) and $J = 4.186 \times 10^7$ ergs per calorie (Art 85), we have $M_v = 2.98$ cals per gram-molecule per $^\circ\text{C}$ for all monatomic gases and is independent of temperature. This prediction is verified by experiment, in the case of argon, for example, the molecular heat is 2.97 at all temperatures.

Remembering the two rotational degrees of freedom possessed by a diatomic gas in addition to its translational energy, we see that the energy U of 1 gram-molecule of the gas at an absolute temperature T is given by

$$U = \frac{5}{2} NkT, \\ \therefore M_v = \frac{dU}{dT} = \frac{5}{2} R$$

$= 4.96$ cals. per gram-molecule per $^\circ\text{C}$. for all diatomic gases and is independent of temperature. This is obeyed by hydrogen at ordinary temperatures, when its molecular heat is 4.84

We shall now calculate the atomic heat of any solid element. In this case the atoms will possess both kinetic energy of oscillation and also potential energy due to their mutual attraction. It can be shown that the average kinetic energy during an oscillation is equal to the average potential energy. Now the oscillations have three degrees of freedom and so the total kinetic energy U_k of 1 gram-atom of the element at an absolute temperature T is given by

$$U_k = \frac{3}{2} NkT$$

Therefore the potential energy U_p is given by

$$U_p = \frac{3}{2} NkT$$

So the total energy U is given by

$$\begin{aligned} U &= 3NkT \\ &= 3RT. \end{aligned}$$

Therefore the atomic heat at constant volume A_v is given by

$$A_v = 3R = 5.94 \text{ cal per gram-atom per } ^\circ\text{C.}$$

for all solid elements, and is independent of temperature. This agrees excellently with Dulong and Petit's law at ordinary temperatures except in the case of carbon, boron, and silicon, but it breaks down completely at low temperatures when the atomic heat tends to zero.

We have now come to the end of the task which we set ourselves at the beginning of this chapter, and we may look back on the results with no little satisfaction. We have succeeded in showing that heat is merely the energy of motion and position of the ultimate particles of matter, a conception which gave great satisfaction to the Victorian physicist, whose sole ambition was to reduce the whole of Physics to mechanics. We have seen that this view of heat is able to explain the properties of the solid and liquid states in a general way, and that it is able to give a comprehensive explanation of the properties of the ideal gas, and therefore of all gases to a first approximation. There is no reason to doubt that it will succeed in explaining the deviations of actual gases from the ideal gas, when the

finite size of the molecules and their mutual attractions are taken into account. But there is a cloud on the horizon. The kinetic theory of matter is completely unable to account for the variation of the specific heat of solids with temperature, and an outline of an alternative and more successful explanation due to Einstein has been given in Chapter II. Is the cloud destined to grow or will it disappear? Does the fault lie with our fundamental theorem of the equipartition of energy, or merely with the way in which we have applied it? For the moment we will leave the matter there to return to it in the conclusion, where we shall attempt to suggest an answer to this interesting question.

EXAMPLES ON CHAPTER IX

1 State the fundamental qualitative facts of heat, and discuss their explanation on the kinetic theory of matter

2 Describe the kinetic theory of gases, and show how the theory explains (a) gaseous pressure, (b) evaporation, (c) the deviation of vapours from obedience to Boyle's law, (d) surface tension (*Camb Schol*)

3 Outline the essential features of the kinetic theory of gases and apply it, so far as you can, to account for the laws of Boyle, Avogadro, and Charles (*Lond B Sc*)

4 Give an account of the simple kinetic theory of gases and deduce a value of the mean square of the molecular velocity. Explain how Boyle's law follows from this theory (*Tripes, Part 1*)

5 Distinguish between the average velocity, most frequent velocity and "root-mean-square" velocity of the molecules of a gas

Calculate the root-mean-square velocity of the molecules of hydrogen and of a gas of molecular weight m at 0°C and 100°C from the following data

Density of hydrogen at 76 cm of mercury pressure and $0^{\circ}\text{C} = 0.0000896$ grm per c.c., density of mercury = 13.6 grm per c.c. (*Lond B Sc*)

6 Give an account of the kinetic theory of gases, explaining how it accounts for the laws expressing the relations between the pressure, volume and temperature of a gas (*Camb Schol*)

7 Deduce an expression for the pressure of a gas from the assumptions of the kinetic theory. Point out clearly the fundamental hypotheses you adopt

Find the square root of the mean square of the velocity of the molecules of nitrogen at 20°C

(Molecular weight of nitrogen is 28, the gas constant R for a gram-molecule is 8.315×10^7 ergs per degree Centigrade (*Trimos*, Part 1))

8 Give a short account of the kinetic theory of gases. If the density of hydrogen at 0°C under pressure of 1033 grm weight per sq cm is 0.09 grm per litre, find the mean square velocity of its molecules at that temperature (*Camb Schol*)

9 On the assumptions of the kinetic theory derive an expression for the "mean velocity" of the molecules of a gas. Show what kind of "mean velocity" must be taken. Calculate this velocity for the case of hydrogen at 0°C and 760 mm of mercury. You may select the appropriate data from the following list

Density of hydrogen = 0.09 grm per litre

Density of mercury = 13.6 grm per c c

Molecular weight of hydrogen = 2

Gram-molecular volume = 22.4 litres (*Camb Schol*)

10 Give a short outline of the Kinetic Theory of Gases. What on this theory is the explanation of (a) the pressure, (b) the viscosity, (c) the conductivity for heat, of a gas? (*Camb Schol*)

11 Give a short summary of the experimental results of the measurement of the specific heats of gases.

Discuss the theoretical explanation of these results (*Camb Schol*)

12 Discuss the way in which the kinetic theory leads to a method of finding the atomicity of gases, illustrating your answer with the various types of case which occur.

13 Give an account of the theorem of the equipartition of energy, and show how it leads to Dulong and Petit's law for the atomic heat of elements in the solid state.

14 Discuss any direct evidence there may be in favour of the fundamental hypothesis of the kinetic theory that the ultimate particles of matter are in rapid and irregular motion.

15 Heat is a "mode of motion" rather than a self-repellent fluid. Discuss this statement.

CHAPTER X

THE RELATION BETWEEN THE LIQUID AND
GASEOUS STATES

109. Introductory.—We have seen in the previous chapter that the kinetic theory is able to give a qualitative explanation of the properties of a liquid and a quantitative explanation of the gaseous state in its simple form at low pressures. But the theory gives no hint of the possibility of a transition from one state to the other, a transition which is very well known in the case of many gases, although there remained the **permanent gases** which had not been liquefied at the time the kinetic theory of gases was first enunciated. There are two possible views which we may take of this state of affairs; we may assert that the permanent gases are essentially different from those which have been liquefied, and that they never can be liquefied, or we may say that the permanent gases are not fundamentally different from the rest, and can be liquefied if only we can attain the necessary conditions of temperature and pressure. The following considerations favour the second point of view:

(a) The gases which have been liquefied show deviations from the ideal gas equation which become less marked as the temperature and pressure get further and further from the point of liquefaction. The permanent gases show very small deviations from the ideal gas equation under ordinary conditions (Art 45). It is possible that these deviations will become more marked at higher pressures and lower temperatures.

(b) We need attach no weight to the fact that the kinetic theory does not lead to any transition from the liquid to the gaseous state, for, in its present form, it explicitly omits the very factor which would lead to such a transition, namely, inter-molecular attractions.

It is now clear that the way to decide between these two possibilities is to make a thorough investigation of the deviations of the permanent gases from Boyle's law and, in the event of their being found, to see if their nature

is such as to suggest inter-molecular attractions. Before giving an account of these experiments, we shall describe one due to Cagniard de la Tour performed in 1822 which has an important bearing on this question

110. Cagniard de la Tour's Experiment.—Cagniard de la Tour tried the effect of heating various liquids such as ether, alcohol, and water in a closed vessel under the pressure of their own vapour. The liquid L was confined to the bulb of a U-tube sealed at both ends by a column of mercury M (Fig 65). The space above the liquid contained only its saturated vapour, while that above the mercury contained air. The whole apparatus was heated up in a suitable oil-bath, as the temperature rose, the liquid evaporated in order to maintain the increased saturation vapour pressure, but no boiling could occur since the liquid was always under the pressure of its own saturated vapour. After a time it was noticed that the meniscus was becoming flatter, and that the distinction between the liquid and its vapour was becoming less and less marked. Then, at a certain temperature, which was different for each liquid, *the meniscus disappeared entirely and the contents of the tube became homogeneous*. It must be emphasised that there was no question of all the liquid having evaporated; that the meniscus did not gradually move to the bottom of the tube. What was observed was that

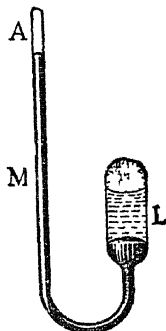


FIG 65.

below this temperature there were two distinct phases or states in the tube, whereas above it there was only one phase, the whole of the liquid and gas having become more and more alike until finally they were indistinguishable. The oil-bath was now allowed to cool and, at very nearly the same temperature, a mist suddenly appeared in the tube and disappeared leaving a faint meniscus once more. These experiments suggested that there was a definite temperature for each substance above which there was no visible distinction between the liquid and gaseous states. We shall call this temperature the **critical temperature** of the substance.

It may be mentioned, in parenthesis, that it is a comparatively simple matter to show this experiment to a class, provided that it is not desired to measure the critical temperature or the corresponding pressure. A thick-walled tube, about 2 mm internal and 4 mm external diameter and 10 cm long, is filled a little more than half full of ether; the air is exhausted by means of a pump and the tube is then sealed off. It is then mounted horizontally over an iron plate and an image of it is projected on to the screen. The iron plate is heated up with a bunsen and the characteristic phenomena occurring at the critical temperature can be seen by the whole class. As the pressure inside the tube at the critical temperature is about 40 atmospheres, both the class and the lecturer should be screened from the tube in case of explosion, although the bursting pressure of a tube of the above dimensions is given as 300 atmospheres.

Faraday continued Cagniard de la Tour's work and succeeded in liquefying a number of gases (Art 119), and he suggested that the reason why the permanent gases could not be liquefied was that their critical temperatures were lower than anything which had ever been reached at that time. This conclusion naturally gave a strong impetus to the study of the isothermals over a wide range of pressure both of gases such as carbon dioxide, which had been liquefied, and of the permanent gases. It would seem the better course to make a thorough investigation of a liquefiable gas first, so we shall now describe the classic experiments of Andrews on carbon dioxide, which were carried out in 1869.

111. Andrews' Experiments on Carbon Dioxide.—

The principle of these experiments is to measure the volume of a fixed mass of gas at various pressures within the range to be investigated. The pressure is calculated from the volume of a fixed mass of air at a fixed temperature subjected to the same pressure as the carbon dioxide, the relation between the pressure and volume for air having already been investigated with the aid of an open-air mercury manometer.

The tube which is to be filled with carbon dioxide consists of a capillary AB leading to a wide bore tube BD

(Fig 66) The two portions of the tube are calibrated by measuring the length of a thread of mercury of known volume at various places while the tube is still open at both ends, and a stream of carbon dioxide is passed through it for twenty-four hours to remove all traces of air. It is then sealed off at A, and a thread of mercury is introduced into the tube by dipping the open end under a bowl of mercury and warming it to drive out a suitable amount of the gas. When the tube is allowed to cool a thread of mercury is drawn into the tube and can easily be manipulated into the position shown. The volume, temperature, and pressure of the gas are now measured, from which its mass can be calculated, and the experimental tube is now mounted in the apparatus for applying the pressure (Fig 67). A second experimental tube is filled with air in the same way, and its volume, pressure, and temperature are also measured before

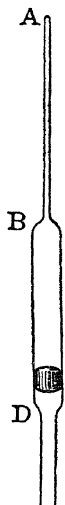


FIG 66

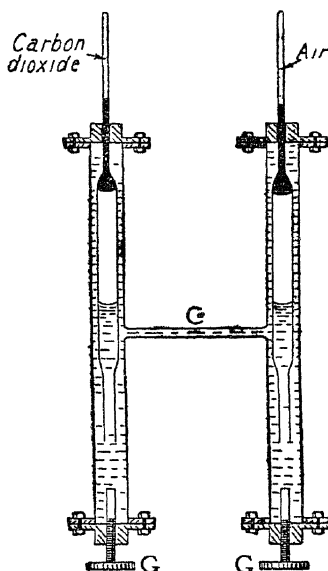


FIG 67

it is mounted in the main apparatus. Each experimental tube is placed in a steel tube filled with water, the pressure of which can be increased by screwing in either or both of the plungers GG. The two tubes are joined by the cross-piece C to ensure that the pressure to which each gas is subjected is the same. Only the capillary portion of the experimental tubes project from the steel tubes, and they are surrounded by a water-bath which is kept at a constant temperature in the case of the air and adjusted to the required value in the case of the carbon dioxide.

The experiment is commenced by screwing in the plungers until the mercury in each tube shows above the steel tube, which occurs at about 30 atmospheres. The volume of each gas is read, and from that of the air, its pressure and therefore that of the carbon dioxide can be calculated. These readings are continued at suitable intervals of pressure until the smallest volume which can be accurately measured is attained. The pressure is then reduced, and a new series of readings at another temperature is obtained

and so on until the requisite range of temperatures and pressures has been explored.

Andrews' results are best understood by considering the graph obtained by plotting the values of p against v for the same temperature. Such a graph is called an **isothermal**, because it refers to the behaviour of the gas at the "same temperature," and Andrews' isothermals for carbon

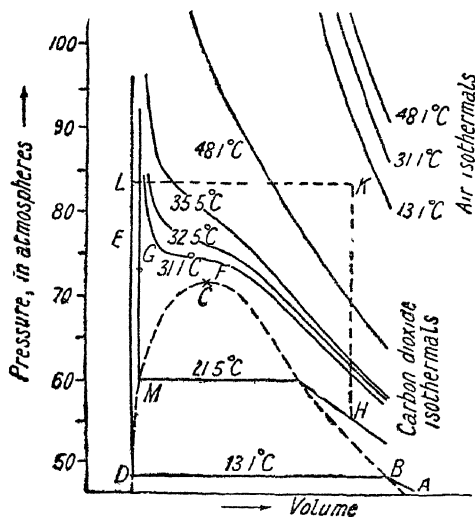


FIG 68

dioxide are shown in Fig 68. Considering the 131°C isothermal first, the portion AB represents the behaviour of the carbon dioxide while it is still a gas, and a quantitative examination shows that it obeys Boyle's law roughly even up to B, the point of saturation. In point of fact, it is rather more compressible than would be expected from this law, which means that pv decreases as p increases. The portion DB of the isothermal corresponds to the change from the gaseous to the liquid state, as is shown by the fact that the pressure of the gas remains constant while the

volume is decreasing, which is the phenomenon of saturation. At D the substance is all liquid, and after that the curve becomes practically vertical since the liquid is almost incompressible. The 21.5°C isothermal shows the same general features, but already two points of difference are significant. Firstly, there is less difference between the volume of the saturated vapour and the liquid, that is, the density of the liquid and its saturated vapour are approaching one another; secondly, the slight departure from the vertical at M shows that the compressibility of the liquid at its boiling point is greater than that at higher pressures and is in fact approaching that of a gas. The measurements also show that the coefficient of expansion of the liquid at its boiling point is increasing as the temperature increases and is approaching the value characteristic of gases. All this suggests that the properties of the liquid and gaseous states are becoming more and more alike and that they will ultimately coincide. This state of affairs is actually realised at the 31.1°C isothermal, which shows no trace of any horizontal portion corresponding to a discontinuous change from the gaseous to the liquid state. Andrews found that the highest temperature at which any noticeable liquefaction occurred and whose isothermal showed a horizontal portion is 30.9°C . The 31.1°C isothermal bears a suggestion of this horizontal portion in the section FG, over which the gas is much more compressible than would be expected if it obeyed Boyle's law. It should also be noticed that the compressibility of the liquid has increased and is rapidly tending to become equal to that of the gas. Isothermals at 32.5°C and 35.5°C . show the same tendencies, although the portion of abnormally large compressibility is becoming less marked and at 48.1°C it has disappeared entirely and the isothermal has become similar to that of a permanent gas, as can be seen from the isothermals for air which are given for comparison. Andrews' results, then, form a striking and complete verification of Cagniard de la Tour's experiment in that they show that the properties of a liquid and its saturated vapour tend to become the same as the temperature increases and do ultimately coincide at a certain value, which we have agreed to call the critical temperature of

the substance. We may accordingly define the critical temperature of a substance as the temperature above which the properties of the liquid and gaseous states are indistinguishable or as the temperature above which the substance does not liquefy. This temperature is therefore 30.9°C in the case of carbon dioxide and the point C in Fig 68 is called the critical point; the pressure and volume corresponding to C are called the critical pressure and volume respectively of the substance.

The similarity between carbon dioxide remote from the critical temperature and the permanent gases can best be realised by plotting the isothermals as $p v$ against p , when they take the form shown in Fig 72. The points to notice are these: firstly, $p v$ decreases as p increases, reaches a minimum, and then increases; secondly, the higher the temperature, the smaller the deviation from Boyle's law becomes, showing that carbon dioxide is becoming more like a permanent gas with rise in temperature. Andrews did not carry his experiments as far as the Boyle temperature, the isothermals in Fig 72 having been plotted from later and more extended experiments.

Further light on the essential continuity of the liquid and gaseous states shown by these experiments can be obtained by considering the following series of changes. Let us start with a given mass of the substance in the state represented by the point H (Fig 68), when it is undoubtedly a gas. Let it be heated at constant volume until the point K is reached and then let it be cooled at constant pressure until the point L is reached. The substance is now all liquid, and yet at no point in the change from the gaseous to the liquid state has any discontinuous change occurred nor would one be seen if the experiment were performed. *We can, in fact, change a substance from the gaseous to the liquid state continuously, and this shows in a very vivid way what is called the continuity of the liquid and gaseous states.* This is yet another example of the fact that Nature knows nothing of sharp dividing lines; they are invariably the creation of the human mind. We may set up the three states solid, liquid, and gas, but there will always be some substances, such as pitch, which are impossible to fit into one or other of these classes, we may speak of metals and

non-metals, but there are certain elements, such as tellurium and selenium, which it is difficult to assign to one class or the other. And in the same way there is no sharp distinction between the liquid and gaseous states in the sense that it is possible to obtain a substance in such a condition that it is difficult to say whether it is a liquid or a gas.

Two important points emerge from these experiments of Andrews. In the first place, they show clearly for the first time the existence of a critical temperature and bring out its real significance. Secondly, they show that the properties of carbon dioxide become more and more nearly identical with those of the permanent gases, the further we go above the critical temperature. Both of these facts favour the view that there is no essential difference between the permanent gases and those which have been liquefied, and with this in mind we must now press on to an investigation of the isothermals of the permanent gases over a wide range of temperature and pressure.

112. Holborn's Experiments on Air and other Gases.—The problem as to whether a particular gas obeys

Boyle's law or not can be solved in one or two ways, which will be clear on a reference to Fig 69. Let us suppose that the graph represents the isothermal of a gas which shows marked deviations from Boyle's

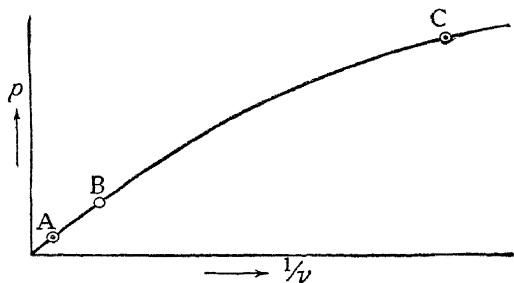


FIG 69.

law. If we confine our investigations to the range of pressure between the points A and B, the departure of the curve from linearity will only be detected by very accurate experiments. On the other hand, if the range of the experiments is extended so as to cover pressures corresponding to the points A and C, the departure from the straight line is much more marked and so will be easier to

detect. The latter method has been invariably adopted and is of course the simpler and more convincing. Our procedure, then, is to increase the pressure up to which we investigate the gas and maintain as great an accuracy as possible.

An increase in range of the experiments introduces two difficulties. If we start with a volume of 100 c.c. at atmospheric pressure, this decreases to about 1 c.c. at 100 atmospheres and obviously cannot be measured accurately. It is evidently useless to extend the range of pressure if the accuracy of the measurements is allowed to decrease at the same time, and so some method must be adopted either of measuring these small volumes accurately or of so arranging the experiments that such small volumes do not have to be dealt with. The second difficulty concerns the measurement of high pressures. Both Regnault and Amagat used the direct method of producing the pressure by a column of mercury of the necessary height and measuring the pressure by finding its height. Amagat, for example, did his experiments at the bottom of a mine and erected a narrow steel tube 327 metres high, with which he could therefore produce and measure a pressure of 420 atmospheres. But among the most accurate experiments performed in this field are those due to Holborn and his collaborators performed in 1915 and in later years, which were carried out over a considerable range of pressure and temperature and for a considerable variety of gases.

The principle of Holborn's method is to measure the mass of gas required to fill a given volume at various pressures. In this way the first difficulty referred to in the previous paragraph is overcome, since the volume of the gas at high pressure is always the same. The mass of gas is measured by allowing it to expand into a series of vessels of known volume until its pressure is about one atmosphere. Its pressure, volume, and temperature are then measured, and from this its volume at N.T.P. and so its mass can be calculated. It is true that in converting the volume of the gas to N.T.P. it is assumed that the ideal gas equation is obeyed, but the pressure and temperature of the gas differ so little from the normal values that the error involved is less than the experimental error. The

high pressure was obtained by a compressor, and was measured by a **pressure balance** designed by Holborn (Fig 70). The pressure of the gas is transmitted by a column of oil to a piston N which moves in a cylinder C. The idea of the oil is to reduce the friction between the piston and the cylinder walls to a minimum, and a slow stream of oil is continually issuing from the top of the cylinder. With the same idea, the piston is kept oscillating to and fro during the time that measurements are being made. The force due to the pressure of the gas is balanced by the weight of the piston, the frame it carries, and weights attached to the frame. In order to avoid any error due to non-uniformity of the cross-section of the cylinder, the piston is always in the same place when the measurements are actually being made. The effective cross-section of the pressure balance is found by means of an open-air mercury manometer and is constant from 1 to 100 atmospheres. At this pressure the balance will detect a change in pressure of 1 mm of mercury, or about $\frac{1}{1000}$ of an atmosphere! It is the most sensitive and accurate instrument which has ever been designed for the measurement of high pressures.

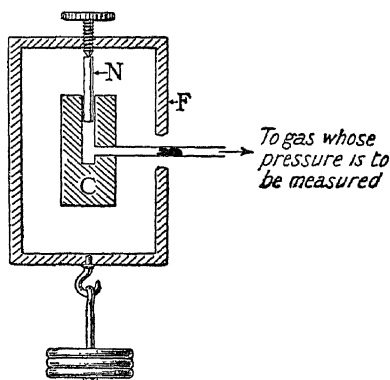


FIG 70

A diagrammatic sketch of Holborn's apparatus is shown in Fig 71. The whole apparatus is exhausted first of all. Then with the tap T_2 closed and T_1 open, the gas under investigation is pumped into the stout glass vessel A until the required pressure is attained. The pressure is at once measured on the pressure balance and the tap T_1 is closed. The vessel A is surrounded by a steel container B nearly full of mercury, which is kept at the same pressure as the gas inside A with a supply of compressed air both for safety and also to avoid having to correct the volume of A.

for the distension due to the pressure of the gas inside it. The whole of A and B is surrounded by a suitable constant temperature bath. As the volume of the flask A and the connecting tubes up to T_1 and T_2 has been accurately determined, we have now measured the volume of the gas at a given temperature and pressure. The mass of the gas is now found by opening the tap T_2 and allowing the gas to expand into the low-pressure side of the apparatus. This includes a set of flasks L_1 , L_2 , L_3 , of known volume, and the gas is allowed to fill a sufficient number of

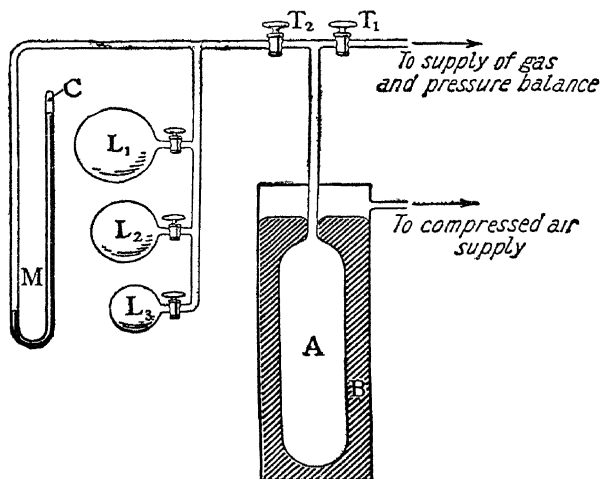


FIG 71

these by opening the corresponding taps until its pressure is nearly atmospheric. There are altogether twelve of these flasks with suitably graded volumes. The actual pressure of the gas is measured by the manometer M, the space C being exhausted, the temperature of the gas is obtained from that of the water-bath surrounding the flasks, and its volume is the sum of that of the vessel A, the various flasks which have been opened, and the connecting tubes, all of which have been accurately calibrated. The volume of the gas at N T P and then its mass is calculated. The low-pressure side of the apparatus is now exhausted

and the tap T_2 is closed and the experiment is now repeated at a different pressure. This is continued until a sufficient range of pressure has been covered, after which the whole process is repeated at a different temperature. When the complete range of temperatures and pressures has been investigated for one gas, the investigation is repeated for the other gases under test.

113. The Results and their Interpretation.—Confining our attention to a given gas at a fixed temperature, we have measured the mass of that gas required to occupy a given volume at various pressures. From these results we can calculate the volume occupied by a fixed mass of that gas at these same pressures, and from this we can work out the variation of pV against p for a given mass of gas at a given temperature. A number of other investigators, notably Kammerlingh Onnes (Art 121), have worked in this field, and their results may be summed up in the equation

$$pV = A + Bp + Cp^2 + Dp^3 + \dots \quad (52)$$

where V is the volume of a gram-molecule of the gas at a pressure p and a fixed temperature. The constants A , B , C , D are characteristic of each gas and they vary with temperature. The constant A is merely RT , and the remainder decrease in magnitude as we go through the alphabet. It is therefore B which is the most important, and it is found that it varies in the same way for all gases, starting with a negative value at low temperatures and increasing to zero at a given temperature and afterwards becoming positive as the temperature rises. This given temperature is called the **Boyle Temperature**, because the gas obeys Boyle's law very closely over a wide range of pressure at this temperature. For example, the Boyle temperature for nitrogen is 50°C , and up to a pressure of 19 atmospheres the gas obeys Boyle's law to 1 in 2000. But at 0°C and 100°C the departures from the law at 19 atmospheres are 7 in a 1000 and 4 in a 1000 respectively.

These results can also be illustrated by plotting isothermals of pV against p (Fig 72). Three important points emerge from the study of these curves.

(a) Above the Boyle temperature, pV increases with p due to the positive value of B , thus the gas is less compressible than would be expected from Boyle's law.

(b) Below the Boyle temperature pV first decreases with p due to the negative value of B and then increases again, and so the permanent gases do show the same type of deviation from the ideal gas equation as is shown by liquefiable gases, such as carbon dioxide

(c) It will be noticed that there are no units on the curves ; this is because the results show that these curves represent the behaviour of all gases in a general way, the only adjustment being that the temperature of any particular isothermal is different for each gas.

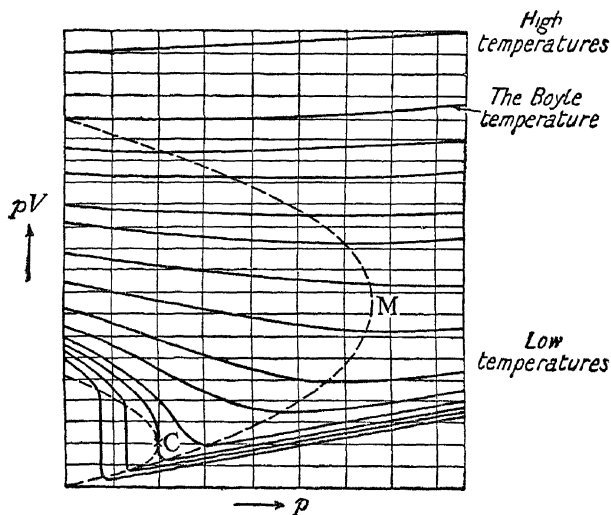


FIG 72

These results suggest that there is no difference between the permanent gases and those which have been liquefied, and we have anticipated their liquefaction for the sake of completeness by including in Fig. 72 those isothermals which refer to the substance in the liquid state. It will be seen that they show precisely the same general characteristics as Andrews' isothermals for carbon dioxide, C being the critical point of the substance.

We must now consider the interpretation of these results

in the light of our problem as to whether there is any essential difference between the permanent gases and those which have been liquefied. The real question is whether these deviations from the ideal gas equation shown by the permanent gases suggest inter-molecular attraction, for this is a property which the molecules must possess if these gases are ever to be liquefied. The fact that, below the Boyle temperature, they are more compressible than an ideal gas suggests the existence of inter-molecular attractions, for they would act in the direction of decreasing compressibility. The increase of pV with p , which sets in at high pressures, suggests that the molecules have a finite size, for it is fundamental that the molecules of matter must repel one another when they are very close. Our experiments show that the molecules do get "very close" at finite pressures and so the molecules must have a finite size. The absence of any decrease of pV with p above the Boyle temperature suggests that either the effect of the finite size of the molecules is greater than that of inter-molecular attraction or that the attraction has changed to a repulsion. The interpretation of the decrease of pV with p as due to inter-molecular attractions is supported by the fact that carbon dioxide shows precisely the same deviation and its molecules certainly attract one another in the liquid state, and a trace of it is likely to be left in the gaseous state when the molecules are further apart.

Our next step in establishing the essential similarity of all gases is to demonstrate *by direct experiment* the existence of these inter-molecular attractions, and also to show that their introduction into the kinetic theory of gases leads to an equation agreeing more closely than the ideal gas equation with the behaviour of all gases over a wide range of temperature and pressure. We shall conclude this chapter with a discussion of the direct experimental evidence for inter-molecular attractions and postpone the theoretical treatment to the next chapter.

114. The Search for Inter-molecular Attraction in Gases.—This problem had attracted Joule's attention as early as 1845 in connection with his experimental determination of the mechanical equivalent of heat by finding the heat produced when air was compressed. Joule saw that

the external work done on the gas would only be equivalent to the heat produced, provided that no work was done by the mutual attractions of the molecules as they approach one another. He had taken no account of this factor in his experiments and was therefore surprised that his value agreed so well with the other experimental results. He decided to seek for these attractions experimentally.

As the principle of all methods of investigating the mutual attraction of the molecules of a gas is the same, it will be as well to deal with it at the outset. It consists of allowing the gas to expand without doing external work and without allowing any heat as such to enter or leave it during the expansion. If the molecules of the gas do attract one another, work will have to be done in pulling them apart, and this can only be obtained at the expense of the heat energy of the gas itself, which will therefore be cooled by the expansion. If the molecules repel one another, the same reasoning shows that the expansion will be accompanied by a rise in temperature, and if there are no intermolecular forces, there will be no change in temperature. We arrive at the same result by using the first law of thermodynamics, which is expressed by equation (44),

$$dQ = dU + dW$$

But, in general, the internal energy of a gas is partly kinetic, due to the motion of its molecules, and partly potential due to their mutual attraction, and the temperature of the gas, it may be emphasised, is proportional to the kinetic energy, not to the total energy, of the molecules. So we may write

$$dU = dU_k + dU_p,$$

where dU_k and dU_p are the increase in kinetic and potential internal energies respectively due to the expansion

$$\therefore dQ = dU_k + dU_p + dW.$$

But since no external work is done and no heat as such enters or leaves the gas during the expansion,

$$\begin{aligned} dQ &= dW = 0, \\ \therefore dU_k + dU_p &= 0, \\ \therefore dU_k &= -dU_p. \end{aligned}$$

That is, if the molecules of the gas attract one another, dU_p is positive, and so the expansion will cause the gas to decrease in temperature

Joule took two small steel vessels A and B joined by a tube provided with a tap (Fig 73). He exhausted B and filled A with air at a pressure of about 20 atmospheres and then immersed them in the minimum amount of water. He stirred the water carefully and noted its temperature on a thermometer sensitive to $\frac{1}{1000}^\circ \text{F}$. He then opened the tap and so allowed the air in A to expand into the vacuum in B, thus doing no external work. The expansion was so rapid that no heat could enter the air or the water-bath from the surroundings and hence a cooling should be observed, if inter-molecular attractions exist. He stirred the water-bath carefully and took its temperature again, but he could never find any difference. He varied the experiment by enclosing A and B in separate water-baths, when it would be expected that the loss in heat in A would be greater than the gain in B, if inter-molecular attractions exist. This unequal distribution of heat is to be expected in this case, since we have divided the air into two parts and that left in A does work on that which is forced into B. Again Joule always found that the heat lost by A was equal to that gained by B, which is what is to be expected if no work is done in pulling the molecules further apart. Joule therefore concluded that if inter-molecular attractions exist, his experiments were too insensitive to detect them. It is worth while emphasising the essential scientific temper of this conclusion, Joule did not commit the blunder of thinking that his experiment was the last word on this question and he stated his conclusion accordingly. He showed that power to suspend judgment in the face of insufficient evidence which is essential to the scientific temper.

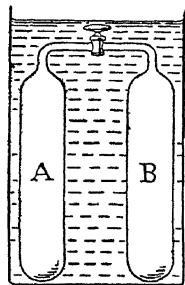


FIG 73

115. The Discovery of Inter-molecular Attractions by the Porous Plug Experiment.—As we have already seen, the evidence is so strongly in favour of the existence

of inter-molecular attractions that Joule decided to make another attempt to show their existence by direct experiment, and he was joined in this attempt by Lord Kelvin. In seeking a new method it is as well to find the reason for the failure of the old one, and a simple numerical example will make this clear. Let us suppose that the vessel A (Fig 73) had a volume of 500 c c, then it would hold about 10 grm of air at 22 atmospheres and room temperature. We shall see at the end of this article that Joule and Kelvin actually found that air suffered a cooling of 5°C when its pressure dropped 21 atmospheres without doing external work. So the heat extracted from the air in Joule's experiment was $10 \times 5 \times 0.17$ (the specific heat of air at constant volume), that is, 10 calories approximately. If the water equivalent of the vessel containing A and B and its contents was 1000 grm, its drop in temperature would only have been $\frac{1}{100}^{\circ}\text{C}$! It is not surprising that Joule failed to detect such a small decrease. This example makes it clear that the thermal capacity of Joule's apparatus was much too big, and Joule and Kelvin overcame this difficulty in an ingenious way by making arrangements to take the temperature of the gas itself.

The principle of their method is to drive the gas by a compressor through a narrow orifice and take the temperature of the gas on entering and leaving the orifice. The apparatus is suitably lagged to prevent any heat as such from entering or leaving the gas during the expansion which accompanies the large drop of pressure as the gas goes through the orifice and no external work is done by the gas, since it does not use its own expansive force to get through the orifice, but is driven through by the compressor. The essential features of the apparatus used for this experiment are shown in Fig 74. The gas is compressed by a suitable machine and is cooled by being passed through a long spiral tube immersed in a cold-water bath W, and its temperature just before entering the orifice is taken by the platinum resistance thermometer T_1 . The gas then enters the orifice, which is the porous plug G made of cotton wool, and suffers a large drop of pressure in passing through it. Its temperature on emerging is read by the platinum resistance thermometer T_2 . The

apparatus is lagged by enclosing the plug in a boxwood tube B, which is surrounded by a brass case L full of cotton wool, which in turn is immersed in the water-bath. A plug of cotton wool is used for the orifice instead of a fine hole in a plate in order to keep down the velocity of flow of the gas on emerging. A subsidiary experiment by Joule and Kelvin with such a hole showed that the velocity of flow on emergence was so much greater than that on entry that it caused a drop in temperature of 1.7°C for each atmosphere fall in pressure.

This is due to the increased kinetic energy of flow of the gas being derived from its heat energy, and as it will mask the effect sought, it must be eliminated in the way which has been indicated.

The procedure in the experiment is to turn on the flow of gas and take its temperature as it enters and leaves the plug when they are steady. It is necessary to wait about an hour for this in order that the flow of the gas may become quite uniform.

Joule and Kelvin's experiment has been repeated for a number of gases over a wide range of temperatures, and it has been shown that the behaviour of all gases is the same. The results of these experiments may be summed up as follows:

- (a) At a low enough temperature all gases show a cooling effect in passing through the porous plug.
- (b) The drop in temperature is proportional to the decrease in pressure.

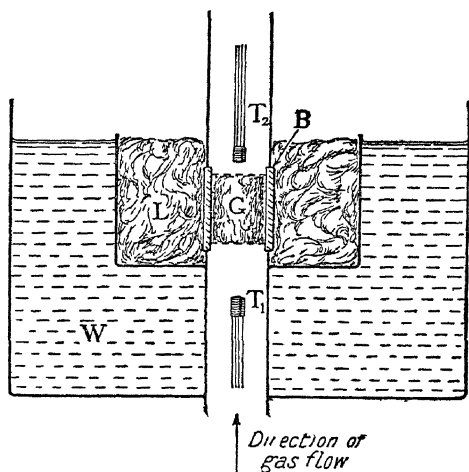


FIG 74

(c) The drop in temperature per atmosphere decreases with rise in temperature, becomes zero at a certain temperature, which is different for each gas, and becomes a rise above that temperature.

This phenomenon is known as the **Joule-Kelvin effect** and the temperature at which it changes sign is called the **temperature of inversion**. The magnitude of the effect is shown by the following results, which apply to 0°C : for air, a cooling of 0.275°C per atmosphere, for carbon dioxide a cooling of 1.39°C per atmosphere, and for hydrogen a heating of 0.03°C per atmosphere

We must now consider these results in the light of inter-molecular attraction. It might seem at first sight as if they show that all gases have inter-molecular attraction below the temperature of inversion, which changes to a

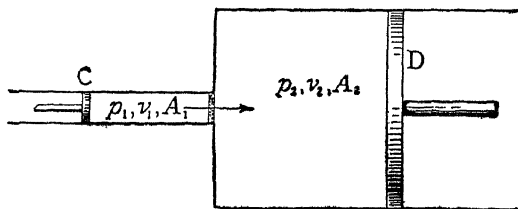


FIG 75.

repulsion above this temperature. But, before jumping to this conclusion, we must be sure that the gas does no external work in being driven through the plug. Let us suppose that the ideally simple arrangement shown in Fig 75 represents the porous plug experiment, the piston C being the compressor driving the gas forward and D taking the place of the pressure of the atmosphere, which is being driven back by the gas. Let p_1 , v_1 , and A_1 be the pressure, volume of unit mass of the gas, and the area of the piston respectively on the high-pressure side, and the same letters with a subscript 2 represent the corresponding quantities on the low-pressure side. Let each piston move a distance x to the right in driving unit mass of gas through the plug, the piston on the low-pressure side having the larger area so that the distance it moves through and

thus the velocity of emergence of the gas is the same as on the high-pressure side. Then the work done on the gas by the compressor is $p_1 A_1 x$ and the work done by the gas against the pressure of the atmosphere is $p_2 A_2 x$. But $A_1 x = v_1$ and $A_2 x = v_2$. Therefore the external work done by unit mass of gas in passing through the plug is $p_2 A_2 x - p_1 A_1 x$, or $p_2 v_2 - p_1 v_1$. Now we know from the experiments of Holborn and others that $p v$ varies with pressure at constant temperature, and the drop of temperature due to passing through the plug will introduce a further variation. We have two cases to consider.

(a) The temperature is below the Boyle temperature and the initial and final pressures and temperatures are such that $p_2 v_2 > p_1 v_1$. In this case the gas does a little external work in passing through the plug and this of itself will produce cooling.

(b) The temperature is above the Boyle temperature. In this case $p_2 v_2 < p_1 v_1$ and so the gas has a little external work done on it, which will produce a rise in temperature.

We see, then, that the Joule-Kelvin effect is made up of two parts, one due to inter-molecular forces and the other due to the small amount of external work done by or on the gas. It is possible to calculate the magnitude of the latter from the experimental data and Holborn's results and so we can find out if there is any effect due to inter-molecular forces. It is found that both the liquefiable and the permanent gases show inter-molecular attraction at least up to the temperature of inversion. At the temperature of inversion itself, which is well above the Boyle temperature, the cooling due to inter-molecular attraction is just balanced by the heating due to external work done on the gas due to deviation from Boyle's law. Above this temperature, the latter effect masks the former, which, however, seems to be decreasing. At any rate, the heating obtained in the case of hydrogen at ordinary temperatures is entirely accounted for by external work and so there is no force between the molecules at this temperature. The deviations from Boyle's law shown by the gas are known to be small under these conditions, and the reason is that they are due solely to the finite size of the molecules. Incidentally the proof of the existence of inter-molecular

attractions makes Mayer's theoretical calculation of the mechanical equivalent of heat illegitimate (Art 83).

116. Conclusion.—We commenced this chapter by enquiring whether it is possible to liquefy the permanent gases or if they really are essentially different from the rest. We have now seen that the permanent gases show precisely the same type of deviation from Boyle's law as the liquefiable gases at conditions remote from the point of liquefaction, we have shown that both classes possess inter-molecular attraction, a condition essential to the realisation of the liquid state; and we have seen that even those gases which have been liquefied possess a critical temperature, above which even they do not liquefy. These conclusions are sufficiently definite to make it almost certain that the permanent gases can be liquefied and to make it worth while to attempt to do so. We are now confronted with the problem of finding the critical temperature of these gases. This is a comparatively simple matter in the case of those which have been liquefied, we can either make a complete investigation of the isothermals as Andrews did for carbon dioxide and from the curves we can read off the critical temperature, pressure, and volume; or we can use Cagniard de la Tour's apparatus, which is much quicker. The critical temperature is found directly, and the reader should be able to see how the critical pressure can be calculated from the saturation vapour pressure of the liquid when cold and the initial and final volume of the air above the mercury and the initial and final difference in levels of the mercury in the U-tube. We shall not enter into the determination of the critical volume, as it involves considerable difficulties owing to the large compressibility of substances near the critical point. But how are we to find the critical constants of a substance which has not been liquefied? It is at this stage in a scientific problem that we call for the aid of theory. Our course is to try to obtain an equation of state which fits actual gases better than the ideal gas equation by taking account of inter-molecular attraction and the finite size of the molecules. If our attempt is successful the equation will lead to the existence of the liquid state, and perhaps we shall be able to calculate from it an approxi-

mate value of the critical temperature We do not require a precise agreement between theory and experiment, because we do not want the exact value of the critical temperature of air, say All we wish to know is whether the critical temperature of air is -100°C or -200°C , so that we may have some idea of the magnitude of the task which confronts us We are about to make a journey into an unknown land and we need a signpost to point the way to the hidden treasure Our signpost is the equation of state of an actual gas, and we shall proceed to its derivation in the next chapter.

EXAMPLES ON CHAPTER X

1 What is the nature of the deviations from Boyle's law of gases, and what explanations have been given of them? (*Tripos*, Part 1)

2. Describe Holborn's experiments on the relation between the pressure and volume of a gas over an extended range of pressures State the general nature of the results he obtained

3 Distinguish between a gas and a vapour

Give an account of the variations from Boyle's law that exist in gases and vapours, illustrating your answer by typical graphs with p and v as ordinates (*Camb Schol*)

4 What is the significance of the gas constant R , and what is meant by a perfect gas?

Describe experiments which have been made to show to what extent actual gases approximate to the ideal perfect gas (*Camb Schol*)

5 Show how Boyle's law is explained on the kinetic theory of gases, pointing out the assumptions that must be made

How far do real gases obey Boyle's law?

6 Discuss the evidence in favour of the existence of the critical point Show how it is possible to change a given mass of substance from a state in which it is all liquid into one when it is all gaseous without both liquid and gas existing simultaneously What bearing has this operation on the relation between the liquid and gaseous states?

7 Discuss the differences in the behaviour of a gas above and below its critical temperature (*Camb Schol*)

8 What is meant by the critical temperature, critical pressure and critical volume of a gas? How can these quantities be determined? (*Camb Schol*)

9 Discuss the relation between the liquid and the gaseous state

Describe some simple method of determining the critical temperature of a substance such as sulphur dioxide. (*O and C*)

10 Give a critical account of the experiments carried out to see if the molecules of a gas attract one another, and discuss the results obtained

11 State clearly what is meant by the Joule-Kelvin effect, and describe briefly how it was established experimentally Give a careful account of the interpretation of the effect

12 Describe and discuss the porous plug experiments of Joule and Kelvin

Explain what is meant by temperature of inversion, illustrating your answer by reference to hydrogen or helium. (*London, B Sc*)

13 Air at 16°C is used in the porous plug experiment between 4000 cm and 76 cm pressure If heat is supplied to the gas as it passes through the plug to keep its temperature constant, find the amount so needed on account of the external work done per gram of air Hence find the drop in temperature of the air if this heat is removed after the air has passed through the plug Will this drop be the same as that measured in the porous plug experiment? Give full reasons for your answer

If the value of pv for air at 16°C and 76 cm pressure be taken as 10000, that at 16°C and 4000 cm pressure is 0.9824; 28.8 grm of air occupy 22.4 litres at N.T.P., and the specific heat of air at constant pressure is $0.24\text{ cal per grm per }^{\circ}\text{C}$.

CHAPTER XI

VAN DER WAALS' EQUATION, AND THE LIQUEFACTION OF GASES

117. Van der Waals' Equation.—We have seen in the previous chapter that experiments over a wide range of pressure show that actual gases deviate from Boyle's law, and that the general nature of the deviations suggests that they are due to mutual attractions between the molecules and the finite size of the molecules. Furthermore, the Joule-Kelvin effect is a direct proof of the existence of inter-molecular forces It is obviously our next step to try to alter our model of the ideal gas in the light of these facts and to see if we can explain these deviations from Boyle's law in the case of actual gases. The first attempt to derive the equation of state of a gas, that is, an equation relating

its pressure, volume, and temperature, was published by van der Waals in 1879. We have to see how the ideal gas equation is modified when it is not assumed that the molecules are of negligible size and exert no influence on one another. We shall consider in the first place the effect of inter-molecular attractions.

Very little is known about these inter-molecular forces except that they are due to some sort of magnetic and electric influence and so must decrease with distance, and we shall assume that each molecule is surrounded by a sphere of influence, such that only molecules inside it can exert any force on it. It is at once evident that a molecule at a point such as D (Fig. 76) is unaffected by intermolecular attractions, since it is being attracted equally in all directions and so the forces merely cancel one another out. Therefore the pressure p_i exerted by the gas on an imaginary plane B is the same as an ideal gas exerts on the walls of the containing vessel and is given by

$$p_i = \frac{RT}{V_i}.$$

But a molecule at E feels a force f due to inter-molecular attractions pulling it away from the wall A of the containing vessel, since its sphere of influence cuts the wall and contains more molecules on the side remote from the wall than on the one near to it. The effect of this force is to decrease the impulse of the molecule on the wall A and so to make the pressure p of the gas less than p_i by an amount α .

$$\therefore p = p_i - \alpha$$

By Newton's third law of motion the effect of the attraction of the walls of the vessel for the molecules of the gas is

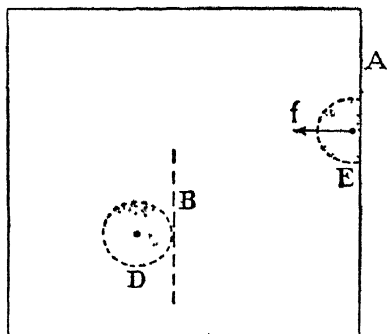


FIG. 76

balanced by the attraction of the gas molecules for the walls of the vessel and so need not be considered. Substituting the value of p_i from the previous equation, we have

$$p = \frac{RT}{V_i} - \alpha,$$

$$\therefore (p + \alpha)V_i = RT$$

To look at the matter from another point of view, the effect of inter-molecular attractions is confined to the molecules in the neighbourhood of the walls of the containing vessel and is equivalent to an external pressure. Therefore in an actual gas it is the sum of the pressure of the walls and that due to inter-molecular attraction which is equal and opposite to that due to the motion of the molecules.

The factor α is evidently governed by the product of the force f on one molecule due to the attraction of the others and the number of molecules striking unit area of the wall per second. Each of these factors is proportional to the number of molecules in unit volume of the gas, or to its density, ρ .

$$\therefore \alpha = c\rho^2$$

where c = a constant for a given mass of the gas.

So we may write

$$(p + c\rho^2)V_i = RT. \quad . \quad . \quad . \quad (53)$$

We shall now consider the finite size of the molecules. This evidently decreases the volume of the space open to them. So an actual gas occupying a volume V is precisely equivalent to one composed of molecules of negligible size occupying a volume V_i , where

$$V_i = V - b$$

A more detailed analysis of the problem shows that b is $4 \times$ the actual volume of all the molecules in the given mass of gas, and not the actual volume itself, as might have been expected at first sight. It is sometimes called the **co-volume** and is a constant for a given mass of the gas. So we can correct for the finite size of the molecules by substituting the above value of V_i in equation (53), which becomes

$$(p + c\rho^2)(V - b) = RT$$

But $p \propto \frac{1}{V}$, so we may write $c\rho^2 = \frac{a}{V^2}$, where a is a constant for a given mass of the gas. So we have

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT, \quad . \quad . \quad (54)$$

which is Van der Waals' equation. We must now see how closely it agrees with the behaviour of actual gases.

118. The Interpretation of the Equation.—Let us suppose that the volume of the gas is decreased n times; then, to a first approximation, the pressure p of the walls of the containing vessel increases n times, whereas that due to inter-molecular attraction, $\frac{a}{V^2}$, increases n^2 times. No matter how much smaller the latter is than the former under ordinary conditions, if n is large enough, it becomes so big that the pressure of the containing vessel is negligible. That is, the gas no longer needs a vessel to hold it, in other words, it has changed to a liquid! Thus Van der Waals' equation explains in a general, but no less striking way, how a gas can change to a liquid.

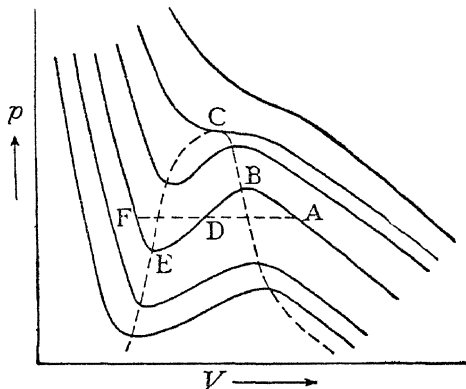


FIG 77

According to the accepted method in scientific work, we shall now turn to the quantitative interpretation of the equation, following the method given in Roberts' *Heat and Thermodynamics*. A family of curves representing the equation is drawn in Fig 77, each curve showing the relation between p and v at constant temperature, the curves corresponding to the highest temperatures being furthest from the origin. We notice that some of the

curves have both a maximum and a minimum, which are absent from those at higher temperatures. Comparing these curves with Andrews' isothermals (Fig 68), we cannot fail to be struck by the general similarity both for the liquid and gaseous states. The disagreement is most marked at the change from the one state to the other, the theory giving the curve ABDEF and experiment the straight line ADF. It should be mentioned, however, that the portions AB and FE have been realised experimentally representing respectively the supersaturated vapour and superheated liquid.

The curve represented by the dotted line is the locus of the maxima and minima of the isothermals, and it is natural to identify the maximum point C of this curve with the critical point of the gas. For, above the temperature represented by the point, an isothermal has neither maximum nor minimum, which means, in practice, that no abrupt change from the gaseous to the liquid state occurs in going along it. Thus the properties of the liquid and gaseous states have merged into one another, in other words the gas is above its critical temperature. We shall now proceed to calculate the critical volume, pressure, and temperature which are represented by the point C. Re-arranging equation (54), we have

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

We find the maxima and minima of the isothermals by differentiating this equation with respect to v and putting the differential coefficient equal to 0

$$\begin{aligned}\therefore \frac{dp}{dV} &= -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0, \\ \therefore \frac{RT}{(V-b)^2} &= \frac{2a}{V^3}\end{aligned}$$

Substituting the value of RT from equation (54) in this equation, we have

$$\begin{aligned}\frac{\left(p + \frac{a}{V^2}\right)(V-b)}{(V-b)^2} &= \frac{2a}{V^3}, \\ \therefore p &= \frac{2a}{V^3}(V-b) - \frac{a}{V^2},\end{aligned}\tag{55}$$

TABLE X

Substance	$\frac{RT_0}{p_0 V_0}$
Helium . . .	3 13
Hydrogen . . .	3 03
Nitrogen . . .	3 42
Argon . . .	3 43
Oxygen . . .	3 42
Carbon dioxide . . .	3 48
Xenon . . .	3 60
Water . . .	4 46
Benzene . . .	3 75
Acetic acid . . .	4 99
Methyl alcohol . . .	4 56

We may sum up the position by saying that Van der Waals' equation succeeds in explaining the deviations from the ideal gas common to all actual gases, but that it breaks down when applied to the differences between the various gases. Other equations of state have been suggested to account for these differences, but they are not conspicuously more successful than Van der Waals' equation, and some of them are open to objection on the ground that the further assumptions they make are empirical, that is, they are designed to produce the right result instead of being deduced from the conditions of the problem.

119. The Liquefaction of Gases.—We are now in a position to make a complete survey of the liquefaction of gases, which may be said to have begun with the liquefaction of chlorine by Faraday in 1823 and to have been completed with the solidification of helium by Professor Keesom in 1926. This subject illustrates the spirit of adventure with which the scientific worker, no less than the explorer, is imbued. The recent expeditions to the Himalayas have been inspired by the challenge which Nature issues to man in the great peaks such as Mount Everest and Kanchenjunga, these lofty heights stand there defying his resource, his endurance, and his ingenuity, and he feels impelled to take up the challenge. And the scientist views

the barriers set up by Nature in the physical world in the same light, and he, in turn, accepts the challenge to his intellectual powers, to his courage, to his determination, and endeavours to triumph over these difficulties. Nature has set the sun and the stars at incredible distances from the earth and separated them from us by empty space to prevent our journeying to them. But this has not prevented the astronomer from taking their temperature, from weighing them, and measuring their size. She has locked up the secrets of the composition and the general properties of matter in a solar system so minute that it is included in a sphere one hundred-millionth of an inch in diameter; but this has not prevented the physicist from inventing microscopes, such as the X-ray spectrometer, and forceps, such as the α -particle, with which he can probe this solar system, which is called the atom. And countless other examples could be quoted from the many other branches of Science. We are concerned here with the challenge which Nature throws down to the mind of man in that some gases can be liquefied and others cannot. She says, in effect, liquefy them all, if you can! And the scientist accepts the challenge, urged on by the desire to obtain complete control over the forces of Nature in this domain. How far he has succeeded will become apparent in the remainder of this chapter.

The history of the liquefaction of gases may be divided into three stages, the first one, which commenced before there was any clear idea of the critical temperature, was not characterised by any very settled plan. The general idea was to cool the gas as much as possible and at the same time apply a large pressure and hope for liquefaction. This was certainly quite a reasonable course, since it was known that a gas such as steam could be liquefied either by cooling or increase of pressure. Faraday liquefied chlorine on these lines and obtained his high pressure in the following ingenious way. He first prepared some crystals of chlorine hydrate, a loose chemical compound of chlorine and water which is unstable at ordinary temperature and pressure, and placed them in a V-shaped stout glass tube, which was then sealed off. He placed the branch of the tube containing the crystals in water and the

other end in a freezing mixture, such as ice and salt. On warming the water, the chlorine hydrate decomposed and emitted a large amount of chlorine gas, which therefore set up a high pressure in the closed tube and eventually liquefied to a yellow oil. Faraday also succeeded in liquefying nitrous oxide, cyanogen, and carbon dioxide on the same lines and he made the further valuable suggestion, after Cagniard de la Tour's experiment became known, that the reason why the permanent gases could not be liquefied was that they were above the critical temperature, yet another example of his amazing insight into physical principles.

The second stage commenced after Andrews had published his experiments on the isothermals of carbon dioxide. This made it clear that no amount of pressure would produce liquefaction if the substance was above its critical temperature, and so the emphasis was now laid on cooling the gas as much as possible. One method which obviously suggests itself is to compress the gas, cool it in a freezing mixture, and then produce a further fall in temperature by the external work done due to a sudden expansion. Cailletet actually succeeded in liquefying oxygen in this way in 1877, and the method has been developed so as to work continuously and produce liquefied gases in quantity. But, almost at the same time and independently, Pictet liquefied oxygen by the **cascade process**, which is continuous and has been developed into a commercial method. It owes its name to the fact that the low temperature is reached in stages. The process commences by liquefying methyl chloride by a compressor; it boils at -24°C . under normal atmospheric pressure and an even lower temperature is reached by allowing it to boil at reduced pressure (Fig 78). The liquid methyl chloride is continually circulating round a condenser through which ethylene is being passed. This has a critical temperature of 10°C . and is easily liquefied in the condenser, and, being made in its turn to boil at reduced pressure in a second condenser, a temperature of -169°C is reached there. This is sufficient to liquefy oxygen, whose critical temperature is -118°C , which, in turn, is boiled under reduced pressure in a third condenser through which air at high pressure

is being passed. The liquid oxygen boils under these conditions at a temperature below the critical temperature of air, which is therefore liquefied. But, at this stage, the method breaks down, for there is no liquefied gas which boils at a temperature below the critical temperature of hydrogen (-240°C). It is therefore necessary to seek for another method of continuously cooling a gas, and the Joule-Kelvin effect suggests itself. We see, at once, that

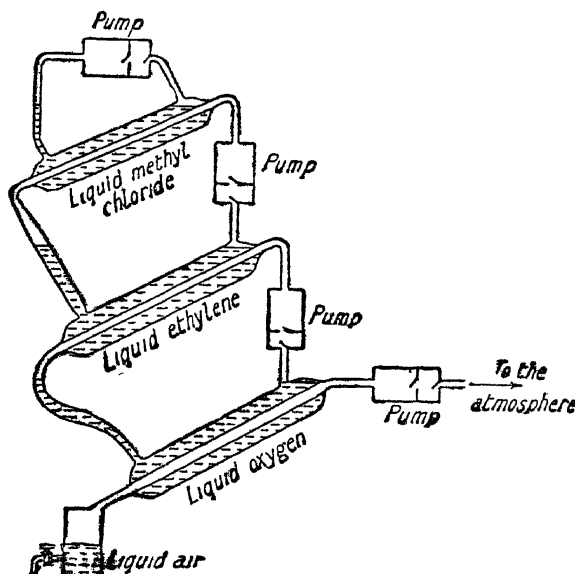


FIG 78.

it will have a considerable advantage over the cascade process even in the case of liquid air, in that much less preliminary cooling is required. In using the Joule-Kelvin effect, it is only necessary to cool the gas below the **temperature of inversion** before applying the effect, but in the cascade process it is necessary to go below the **critical temperature**, which is always much lower than the temperature of inversion. In fact, if the substance obeys

Van der Waals' equation, it can be shown that T_i , the temperature of inversion, is given by

$$T_i = \frac{2a}{Rb} \quad . \quad . \quad . \quad (59)$$

Combining this with equation (58) for the critical temperature, we have

$$\frac{T_i}{T_c} = \frac{2a}{Rb} \bigg/ \frac{8a}{27Rb} = \frac{27}{4}.$$

Hence we see that the Joule-Kelvin effect is likely to be a much more convenient method of liquefaction than the cascade process. With air no preliminary cooling is necessary, and with hydrogen, our immediate objective, it is only necessary to cool below -80°C . This method was first applied by Linde to air, and we shall now describe the principles of his apparatus and its further application by Dewar and Kammerlingh Onnes to hydrogen and helium respectively.

120. Linde's Method for Air and Hydrogen.—The air is compressed to about 200 atmospheres, cooled by passing through a cold-water bath, freed from carbon dioxide and water vapour by passing it through caustic potash, calcium chloride, and phosphorus pentoxide tubes respectively. This last precaution is necessary since the water vapour and carbon dioxide would solidify before the air liquefied and block the circulation system. The air now enters the liquefying apparatus proper at A and passes down through a tube which is really a spiral to the nozzle N, where it suffers a drop in pressure, the magnitude of which can be controlled by a valve (not shown in Fig 79). It issues from the nozzle at about 20 atmospheres, it has therefore undergone a considerable expansion and will have suffered a considerable drop in temperature due to the Joule-Kelvin effect. For air and the above drop of pressure, the fall in temperature is about 40°C . This cold air now leaves the apparatus by the tube B, which is built round the outside of the inlet pipe, and so it cools the next lot of incoming air, which therefore reaches and issues from the nozzle at an even lower temperature. As the circulation continues, the air is therefore cooled more and more until it is below the critical temperature, and soon after

that liquefaction sets in. The outgoing air is either allowed to escape to the atmosphere or led back to the compressor again in the case of other gases. The liquid air is drawn off as required by opening the tap T and is collected in a Dewar flask, which is just like a thermos flask. The whole of the liquefying apparatus is well lagged with cotton wool L in order to prevent the air from receiving heat from its surroundings as fast as it loses it by the Joule-Kelvin effect.

It was in 1895 that Linde first succeeded in liquefying air by this method, and he was followed very closely by Dewar, who used it to liquefy hydrogen in 1898. It is necessary to cool the hydrogen below the temperature of inversion before applying the Joule-Kelvin effect, which is now done by passing the gas through liquid air boiling under reduced pressure. Dewar afterwards solidified hydrogen by boiling the liquid under reduced pressure, reaching in this way a temperature of -259°C . Both the liquid and solid are colourless and transparent.

121. Kammerlingh Onnes' Work on Helium.

Work on Helium.—We now come to the case of helium, which was the last gas to be liquefied. This was attacked by Kammerlingh Onnes, and in view of the failure which had attended other attempts on this gas, he decided to investigate its deviations from Boyle's law at high pressures and low temperatures in order to be able to calculate the a and b of Van der Waals' equation. By substituting these values in equations (58) and (59), he could calculate the critical temperature and temperature of inversion respectively. He obtained several values of each quantity in this way, and they did not agree particularly well, probably because helium does not obey Van der Waals' equation. But his results

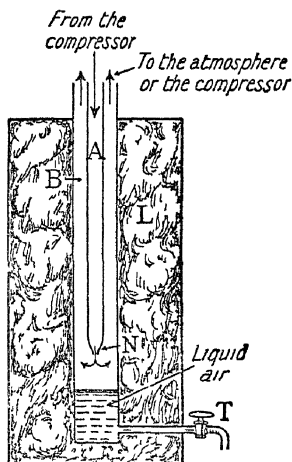


FIG 79

showed that the temperature of inversion was greater than that which could be reached with liquid hydrogen boiling under greatly reduced pressure, so he decided to try Linde's method. Kammerlingh Onnes spent some ten years on this preliminary work, but the results justified the labour, since he succeeded in liquefying helium in 1908. He passed the pure compressed helium through liquid hydrogen boiling at reduced pressure. In this way he reached a temperature of -258°C and then he applied the Joule-Kelvin effect. He found that the critical temperature of the gas is -268°C and its boiling-point under normal atmospheric pressure is -268.8°C . Recalling what we said in Art. 116 about the possibility of calculating the critical temperature of the permanent gases by means of an equation of state, we see that this is just what Onnes has done, although it must be said that this is the only case where the method was applied. But the truly scientific nature of Kammerlingh Onnes' attack on this most difficult problem cannot be too strongly emphasised, he did not go forward blindly with the Joule-Kelvin effect, trusting to Providence that he would reach his goal, but spent many years of careful experimental work in order to satisfy himself that the method was feasible. And it is a tribute to his courage that he was not turned aside from his purpose by his predictions of the values of the critical temperature and temperature of inversion, which were so low as to suggest the gravest difficulties.

Kammerlingh Onnes then turned his attention to the solidification of helium, but this he was not destined to accomplish. No doubt he hoped to succeed by boiling the liquid under reduced pressure, but although he reached a temperature of 1°A in this way, the helium still remained in the liquid state. It fell to his successor, Professor Keesom, to complete this task, and he succeeded in doing so in 1926, when he produced solid helium at a temperature of 3.2°A and a pressure of 86 atmospheres. He proved the existence of the solid in two ways, the first one consisted in showing that a circulating system for the liquid had become blocked, and the second one consisted in actually hammering the solid in a tube with a magnetic hammer. The tube containing the liquid was visible, and the liquid

was agitated with a magnetic stirrer while it was being cooled and pressure was being applied. After a time it was seen that the stirrer was becoming more sluggish, until finally it could not be moved, the inference being that the helium had solidified. Again, if only the liquid in the lower part of the tube were frozen, the stirrer could be made to move up and down and could be seen hammering the solid, which revealed its presence in this way, for it could not be distinguished visually from the liquid. So it evidently has the same refractive index as the liquid.

Before leaving this interesting subject it is as well to point out that its practical applications have turned out to be as fruitful as its development is interesting. The standard way of preparing oxygen on the commercial scale is by the liquefaction and subsequent fractional distillation of air; the rare gases of the atmosphere, whose uses have been enumerated in Art 68, are isolated by the same process, an up-to-date colliery possesses a liquid air plant in order that there may be a plentiful supply of oxygen in the event of an explosion. Finally we are able to reproduce in the laboratory low temperatures and therefore conditions identical with those in the upper atmosphere, and so we can study its properties at leisure.

EXAMPLES ON CHAPTER XI

1 Give some account of experiments made to test Boyle's law over large ranges of pressure. How are these experiments interpreted in the light of the kinetic theory of gases? (*Camb Schol*)

2 Discuss the departure of gases from Boyle's law, and the explanations which have been given of them.

Give a rough sketch showing the general shape of the isothermals on Van der Waals' theory that

$$\left(p + \frac{a}{v^2}\right)(v - b) = R\theta. \quad (\text{Camb Schol})$$

3 Compare the behaviour of an ordinary gas with that of the "Perfect" gas. Give reasons for the main differences (*Camb Schol*)

4 The equation $p v = RT$ represents the behaviour of a perfect gas Give some account of the deviations from this law which are found experimentally, and describe how they are explained in Van der Waals' equation (*Camb Schol*)

5 Why do real gases not obey Boyle's law ?

Obtain relations between the critical constants of a gas and the constants of Van der Waals' equation (*Oxford Schol*)

6 Explain how Van der Waals' equation is obtained, and use it to derive an expression for the critical temperature of a gas (*Tripos, Part I*)

7 Explain why a vapour does not obey Boyle's and Charles' laws, and show how Van der Waals' equation allows for the two principal causes of divergence from these laws (*Camb Schol*)

8 What is meant by the critical temperature of a substance ?

Explain the principle of the usual method of cooling air below its critical temperature (*Camb Schol*)

9 Give a short account of experimental methods of obtaining and measuring very low temperatures (*Camb Schol*)

10 Give an account of the methods of liquefying gases and discuss the principles on which these methods depend (*Tripos, Part I*)

11 Give a description of the method generally employed in the manufacture of liquid air (*Camb Schol*)

12 Describe fully one method of liquefying a gas

State clearly the principle underlying the method, and explain how the temperature of liquefaction may be measured (*Camb Schol*)

13 Describe the methods employed in the liquefaction of (a) air, (b) hydrogen

How are very low temperatures measured ? (*Camb Schol*)

14 Describe the principle on which the liquefaction of air depends Given a supply of liquid air, how could liquid and solid hydrogen be obtained ? (*Oxford Schol*)

15 Give a critical account of the liquefaction and solidification of helium, paying especial attention to the way in which the initial stages of the problem were tackled

16 Man can only obtain control over Nature by a patient and diligent study of her laws for their own sake Discuss this statement with special reference to the liquefaction of gases.

CHAPTER XII

CYCLICAL OPERATIONS AND ADIABATIC CHANGES

122. Introductory.—We have seen in Chapter VIII that heat is a form of energy and can be included in the generalisation known as the conservation of energy. This means that conversions from work into heat or vice versa are governed by the condition that the quantities of heat and work involved are always equivalent to one another. This is the First Law of Thermodynamics. Now, it is only too easy to convert work into heat, this change is the bugbear of the engineer, in that it compels him to reduce friction to a minimum by constructing his bearings with care and providing for their efficient lubrication. But the consideration of paramount importance and interest for him is the production of mechanical work from other forms of energy, among which heat at once suggests itself. The question arises as to whether any laws govern this transformation other than the First Law of Thermodynamics. We shall proceed to the consideration of this matter in the next chapter, dealing at the moment with one or two points which have to be cleared up before the chief problem can be tackled. Accordingly we proceed to the consideration of **cyclical operations** and later to **adiabatic changes**.

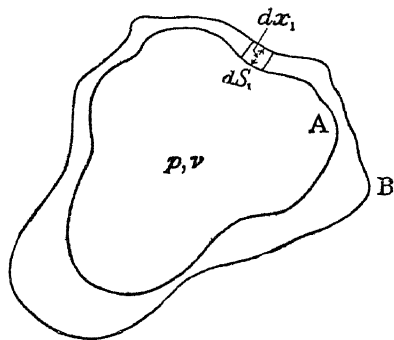


FIG 80

123. Work Done in Expansion.—Let a given mass of the substance, which may be a solid, liquid, or gas, be contained in a vessel represented by A (Fig 80). Let the pressure exerted by the substance on the walls of the vessel be p and its volume v . Let us suppose that the substance now suffers a very small expansion to the shape B. Then,

considering the element of area dS_1 shown in the figure, the force on it due to the pressure of the substance is $p dS_1$. Since it moves through a distance dx_1 , the work done is $p dS_1 dx_1$, the pressure being constant because the change in volume is very small. Therefore the total work done by the substance in expanding is $\sum p dS_1 dx_1$ or $p \sum dS_1 dx_1$, where the summation is taken over the whole surface of the substance. But $\sum dS_1 dx_1 = dv$, where dv is the increase in volume due to the expansion. Therefore the work done by the substance in expanding $= p dv$. If the expansion occurs at constant pressure and the volume increases from v_1 to v_2 , the total work done $= p(v_2 - v_1)$, and is represented on a graph of pressure against volume of the change by the

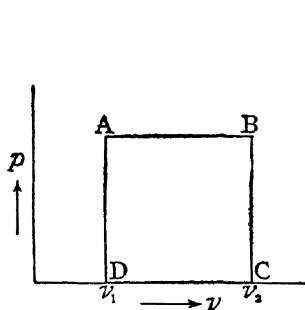


FIG 81.

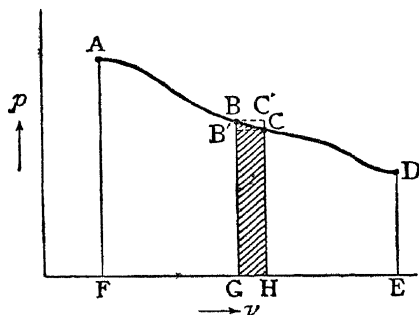


FIG 82

area ABCD (Fig 81). Such a graph is called an indicator diagram.

If the pressure changes during the expansion, the work done in a finite change of volume can be deduced quite simply. Let us suppose that the changes of pressure and volume suffered by the substance are represented by the indicator diagram drawn in Fig 82. Let us consider the infinitely small expansion represented by BC. The work done by the substance in this expansion lies between the area of the two rectangles $BC'H'G$ and $B'CHG$. As the increase in volume GH is made smaller and smaller, these two areas become as nearly equal as we please to the area $BCHG$. That is, in the limit, the work done by the substance is equal to the area $BCHG$. Now the work

done by the substance in the finite expansion as it goes from A to D is evidently equal to the sum of all the areas corresponding to BCHG, that is, the area ABCDEFA. It should be emphasised that this is the area between the *curve* ABCD, the volume axis, and the two ordinates at the extremities of the indicator diagram. This result obviously reduces to the one already obtained in the previous paragraph in the simpler case when the pressure remains constant.

Mathematically, the work done by a substance in expanding from a volume v_1 to v_2 is given by

$$W = \int_{v_1}^{v_2} p \, dv,$$

which is precisely equivalent to the graphical result. If the pressure remains the same, $W = p(v_2 - v_1)$, agreeing with the previous result for constant pressure.

124. Cyclical Operations.—We are now in a position to consider the characteristics of cyclical operations which are of fundamental importance in thermodynamics. Let us suppose that a given mass of substance is contained in a cylinder closed by a piston, and that it is taken through the series of changes represented by ACB (Fig 83). The external work done is given by the area ACBEFA, but this is not in general equal to the heat absorbed, since the internal energy of the substance is different at B from what it is at A. Hence from equation (44), which expresses the first law of thermodynamics, we have

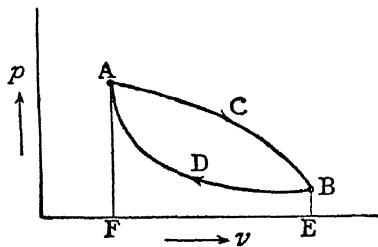


FIG 83

$$Q = (U_B - U_A) + \text{Area ACBEF}$$

where Q is the heat absorbed by the substance in going from A to B and U_A and U_B are its internal energies at A and B respectively.

If U_B is greater than U_A , some of the heat absorbed will go to supply this increase of internal energy, and so the external work done will be less than the heat absorbed. Now, in thermodynamics, we are interested mainly in the connection between these last two quantities, and it is impossible to express this in a simple mathematical form for a change of the sort outlined above, since we have not got a simple expression relating the internal energy of a substance and its pressure, volume, and temperature. If the substance is an ideal gas, the change in internal energy takes the very simple form $C_v dT$, because there are no inter-molecular forces and so it is independent of any change in volume; but if we make the trifling change to an actual gas, there is no simple expression relating the change in the internal energy and the changes in its temperature and volume, say. But we do know that the internal energy of any substance is some function of the pressure, volume, and temperature, that is, when these three quantities are specified, so is the internal energy. But there is also some relation between the pressure, volume, and temperature for any substance; it is the ideal gas equation for the ideal gas, for example, or Van der Waals' equation for an actual gas. Therefore only two of these quantities are independent. Hence we may say that the internal energy of a substance is fixed when its pressure and volume are specified. **This means that the internal energy of a substance is always the same when its condition is represented by the same point on an indicator diagram**; if it starts from a given condition and is brought back to that same condition, its internal energy will be the same no matter what changes it may have undergone in the meantime. It follows that the change in internal energy of a substance in going from A to B (Fig 83) is quite independent of the path by which it goes from one point to the other; it is the same whether it goes via C or D. It is important to contrast this with the external work done, which is given by the area ACBEFA in the first case and the area ADBEFA in the second.

We can now resume our argument concerning the interchange between heat and work. Let us suppose that we take our substance contained in a cylinder with a piston

through the cycle of changes represented by ACBDA (Fig 83), the term cycle is used here because the substance ends in the same condition as regards pressure, volume, and temperature as it started. Applying the first law of thermodynamics, we have

Net amount of heat absorbed in the cycle = the increase in internal energy + the external work done

But the increase in internal energy is zero, since the initial and final states of the substance are the same. Also the external work done by the substance in going from A to B via C is the area ACBEFA, and that done on the substance in going from A to B via D is the area ADBEFA. So the net external work done by the substance in the cycle is the difference of these two areas, which is the area of the closed cycle itself, ACBDA. So in the case of a cyclical operation, we have

Net amount of heat absorbed = the external work done
= the area enclosed by the cycle

It must be emphasised that although the change of internal energy is the same whether the substance goes from A to B via C or D, the heat absorbed is not, being greater in the former case, since the external work is the greater. It will also be seen that we have succeeded in obtaining a direct relation between work done and heat absorbed without bringing in internal energy by making use of a cyclical operation. We shall appreciate the importance of this in the next chapter.

125. Adiabatic Changes.—Let us suppose that we have a given mass of a substance enclosed by a piston impervious to heat in a cylinder, whose walls are perfect heat insulators and whose bottom is a perfect conductor. If the cylinder is now placed in contact with a source of heat of infinite thermal capacity at a temperature T and the substance is allowed to expand by slightly decreasing the external force on the piston, external work will be done by the substance, but an equivalent amount of heat will flow into it as its temperature must remain the same as that of the source of heat. Such an increase in volume is called an isothermal change and we are quite familiar with them and have studied the relation between the pressure

and volume of gases under such conditions. Now let us replace the perfectly conducting bottom of the cylinder by one made of a perfect insulator and repeat the expansion. External work will again be done, but as the substance is thermally isolated, it must draw on its own heat supply for this and so it cools itself as it expands. This type of change is called an adiabatic change, and may be defined as one which is subject to the conditions that no heat as such enters or leaves the system, and that the system only departs by an infinitesimal amount from equilibrium with the external forces acting on it. This does not imply that the heat content of the system remains constant during the change, on the contrary, it will usually alter, as in the example outlined above, since the external work accompanying the change has to be drawn from the heat energy of the system. It means that no heat flows by conduction into or out of the system. The condition that the system shall be very 'nearly in equilibrium with the external forces implies that the change is **reversible**, which is a technical term whose implications are fully discussed in the next chapter (Art 137). The reader is advised not to pay very much attention to this aspect of the adiabatic change until he has studied reversibility, after which he should return to the full consideration of adiabatic changes. Sound waves are perhaps the only perfect adiabatic change ever realised in practice. In this case the compressions and rarefactions of a given mass of air take place so rapidly, 256 times a second in the case of middle C, that there is no time for the heat developed in the compression to flow to the neighbouring rarefaction. Again, if the valve of a motor-car tyre is removed, the expansion of the air leaking out of the tyre is approximately adiabatic; at any rate, it is cooled sufficiently to be detected by the hand.

It can easily be shown that the slope of an adiabatic is greater than that of an isothermal at the point where they cross on the indicator diagram. In Fig 84 three isothermals of any substance for the temperatures $T - dT$, T , $T + dT$ are drawn, the only assumption made as to the behaviour of the substance being that it expands with rise of temperature and that the volume decreases with increase of

pressure, which is necessary for stability. Let us consider the adiabatic through the point B. If the substance suffers an adiabatic expansion starting from the state represented by the point B, the external work done causes its temperature to fall and so the adiabatic curve must descend to the $T - dT$ isothermal and cross it at the point C, say. In the same way, if it undergoes an adiabatic compression, its temperature rises and so it must reach the $T + dT$ isothermal and cross it at A, say.

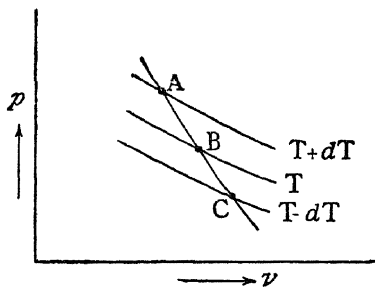


FIG 84

So ABC is the adiabatic through B, and its slope is greater than that of the isothermal at the point where they cross. It must be emphasised, in conclusion, that this result is true for any substance, solid, liquid, or gas, since we have made no assumption as to the shape of the isothermals.

126. The Equation to an Adiabatic for an Ideal Gas.—We shall first derive the equation for an adiabatic change of any substance, which can be done if we bear in mind two principles

(a) The change must satisfy the First Law of Thermodynamics.

(b) It must satisfy the condition that no heat as such enters or leaves the substance during the change.

The first principle is expressed mathematically by the familiar equation

$$dQ = dU + dW, \quad . \quad . \quad . \quad (60)$$

where the symbols have their usual meaning. From the second principle, we have

$$dQ = 0$$

Substituting this value of dQ in the previous equation, we have

$$dU + dW = 0, \quad . \quad . \quad . \quad (61)$$

which is the general equation to an adiabatic change of any kind for any substance

If we now consider the particular case of a change in volume of an actual gas, the external work takes the form of work done against a piston enclosing the gas in a cylinder or against the atmosphere. So we have

$$dW = p \, dv,$$

where p is the pressure of the external force opposing the expansion and dv is the adiabatic increase in volume. Since the change is reversible, this external pressure is only an infinitesimal amount less than the pressure of the gas. Substituting this value of dW in equation (61), we have

$$dU + p \, dv = 0 \quad . \quad . \quad . \quad (62)$$

This equation can now be developed by substituting for dU some expression in terms of the temperature and volume, say, for the porous plug experiment shows the existence of inter-molecular forces in actual gases and therefore that the internal energy depends on the volume as well as the temperature. There are a number of alternative expressions which may be chosen according to the particular equation of state selected, but none of them leads to a particularly simple result and the matter will not be considered further in this book.

But the case of the ideal gas leads to a simple result, as may be expected. Since there are no inter-molecular forces in such a gas, the internal energy consists solely of the kinetic energy of the molecules and depends only on the temperature. In fact $dU = C_v \, dT$, if we consider unit mass of the gas, where C_v is the specific heat at constant volume of the gas and dT is the change in temperature corresponding to the adiabatic change in volume dv . Substituting this value of dU in equation (62), we have

$$C_v \, dT + p \, dv = 0 \quad . \quad . \quad . \quad (63)$$

This is the equation to an adiabatic for an ideal gas. But it can be simplified still further by eliminating either the pressure, volume, or temperature with the aid of the ideal gas equation

$$pv = rT, \quad . \quad . \quad . \quad (63a)$$

which must be satisfied by any kind of change of an ideal gas. Here p is the pressure of the gas, but since adiabatic changes are reversible, it is equal to the external pressure p of equation (62), and so the same letter may be used for either quantity. It must be emphasised that this is only the case because adiabatic changes are reversible, by definition. Differentiating equation (63a), we have

$$p \cdot dv + v \cdot dp = r \cdot dT \quad . \quad . \quad (64)$$

Substituting the value of dT from this equation in equation (63), we have

$$\frac{C_v}{r} (p \cdot dv + v \cdot dp) + p \cdot dv = 0,$$

$$\therefore C_v \cdot p \cdot dv + C_v \cdot v \cdot dp + r \cdot p \cdot dv = 0.$$

But from equation (43),

$$C_p - C_v = r.$$

Substituting this value of r in the previous equation,

$$C_v \cdot p \cdot dv + C_v \cdot v \cdot dp + C_p \cdot p \cdot dv - C_v \cdot p \cdot dv = 0,$$

$$\therefore C_v \cdot v \cdot dp + C_p \cdot p \cdot dv = 0,$$

$$\therefore \frac{dp}{p} + \frac{C_p}{C_v} \frac{dv}{v} = 0,$$

$$\therefore \frac{dp}{p} + \gamma \frac{dv}{v} = 0 \quad \text{where} \quad \gamma = \frac{C_p}{C_v}.$$

Integrating, we have

$$\log p + \gamma \log v = \text{constant}.$$

$$\therefore p v^\gamma = \text{constant}. \quad . \quad . \quad (65)$$

The corresponding relations between v and T or p and T are obtained by eliminating p or v respectively from equation (65) by means of the ideal gas equation and are given below

$$T \cdot v^{\gamma-1} = \text{constant}, \quad . \quad . \quad (66)$$

$$\frac{p^{\gamma-1}}{T^\gamma} = \text{constant}. \quad . \quad . \quad (67)$$

These are the equations to an adiabatic of an ideal gas and they may be used without appreciable error in the case of any actual gas under conditions remote from the point

of liquefaction. If we differentiate equation (65), we obtain

$$\frac{dp}{dv} = -\gamma \frac{p}{v}.$$

Differentiating the equation to an isothermal, $pv = \text{constant}$, we have

$$\frac{dp}{dv} = -\frac{p}{v}$$

Since γ is always greater than 1, this shows that, in this particular case, the numerical value of the slope of an adiabatic is greater than that of an isothermal at the point where they cross, a result which we have previously shown to be true of all substances.

We shall illustrate these equations by a numerical example. Let us calculate the drop in temperature of the air in a motor-car tyre pumped up to 2 atmospheres at 15° C. when it bursts, the consequent expansion being assumed adiabatic. From equation (67), we have

$$2^{\gamma-1}/288^{\gamma} = 1^{\gamma-1}/T^{\gamma},$$

where T is the final absolute temperature of the air. Taking γ for air as 1.4, we have

$$T = 232^{\circ} \text{ A or } -41^{\circ} \text{ C.}$$

So the drop in temperature of the air is 56°.

127. The Determination of the Ratio of the Specific Heats of a Gas : Clément and Désormes' Method.—

The most obvious way of finding the ratio of the specific heats of a gas is to calculate it from the values of C_p and C_v found by direct experiment. But the fact that the equation to an adiabatic for an ideal gas involves γ suggests that it may be possible to devise a method of finding it directly by using an adiabatic change, and it is of interest to state that such a method was actually devised before the direct method of finding C_v had been evolved by Joly and the value obtained for γ was used to work out C_v from the known value of C_p . But it is important to have a number of independent ways of finding γ , because we have already seen that a knowledge of its value enables us to decide the atomicity of a gas.

The methods of determining γ which make use of adiabatic changes may be divided into two classes, those which use the natural adiabatic changes accompanying sound waves and which will be treated in Art 131, and those which use an artificial adiabatic change. The principle of this second class, of which two varieties will be described, is to cause a given mass of gas at a pressure p_1 and absolute temperature T_1 to undergo an expansion, which is as far as possible adiabatic, to a pressure p_0 and absolute temperature T_0 . From equation (67), we have

$$\frac{p_1^{\gamma-1}}{T_1^{\gamma}} = \frac{p_0^{\gamma-1}}{T_0^{\gamma}} \quad \text{or} \quad \left(\frac{p_1}{p_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^{\gamma} \quad (68)$$

from which γ can be calculated by taking logarithms, if the initial and final pressures and temperatures have been measured

The obvious difficulty in the realisation of this experiment is the measurement of the final temperature. For the only way of realising an adiabatic expansion in practice is to make it take place very quickly under the best possible conditions of heat insulation. As soon as the expansion is over, heat will inevitably be conducted into the system and the longer we wait, the more heat will enter. So it is essential that the temperature should be measured immediately the expansion is completed and that the time occupied in the measurement should be as short as possible, since it is rising the whole time. At the beginning of the nineteenth century, when interest in γ was first aroused, such a thing simply could not be done, but Clément and Désormes avoided the necessity of doing it in a most ingenious way. They followed the adiabatic change by an increase in pressure at constant volume until the gas had risen to its original temperature once more. If p_2 is the final pressure reached by the gas in this way, since the change takes place at constant volume, we have

$$\frac{p_2}{p_0} = \frac{T_1}{T_0}$$

Substituting this value of $\frac{T_1}{T_0}$ in equation (68), we have

$$\left(\frac{p_1}{p_0}\right)^{\gamma-1} = \left(\frac{p_2}{p_0}\right)^{\gamma}.$$

Taking logarithms,

$$(\gamma - 1)(\log p_1 - \log p_0) = \gamma(\log p_2 - \log p_0),$$

$$\therefore \gamma = \frac{\log p_1 - \log p_0}{\log p_1 - \log p_2}, \quad \dots \quad (69)$$

from which γ can be calculated if the three pressures p_1 , p_0 , and p_2 have been measured,

The gas under investigation was contained in a large flask at a pressure a little greater than atmospheric, its actual value being measured with an oil or sulphuric acid manometer (Fig 85). A water manometer must be avoided otherwise the gas will become contaminated with water vapour, and we shall be measuring the value of γ for a mixture of the gas and water vapour instead of for the pure gas. A large flask is used to reduce the loss of heat

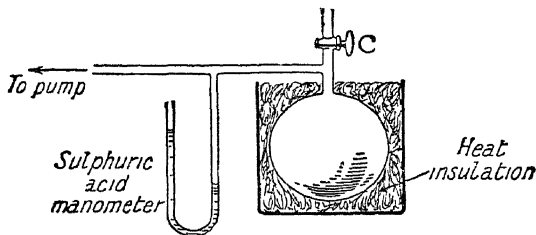


FIG 85.

by convection and conduction to the gas from its surroundings as much as possible, the loss of heat is proportional to the surface of the flask or to the square of its radius, whereas the mass of gas in it is proportional to its volume or the cube of the radius and so the bigger the radius, the smaller the cooling per gram of gas. To the same end the flask is surrounded by a large amount of straw or cotton wool and by this means the conditions for an adiabatic change are realised as nearly as possible. The expansion is reversible because the decrease in pressure is arranged to be small, and the gas as a whole acquires only a small velocity. The procedure in the experiment is to measure the initial pressure p_1 of the gas and then to open the tap C and close it again quickly. This tap is of wide bore and so the expansion to atmospheric pressure p_0

takes place quickly. This fact, together with the precautions described above, ensures that the expansion is adiabatic. The gas is now left to warm up to the temperature of the surroundings once more, its pressure rising in the process. The highest pressure p_2 reached by the gas is read on the manometer and the value of γ is calculated from p_1 , p_2 , and p_0 by means of equation (69).

The results obtained by this method were not as consistent as might have been expected, until it was pointed out that it was open to one serious objection. When the gas falls to atmospheric pressure on opening the tap C, a series of oscillations will be set up on account of its inertia. When the pressure of the gas has decreased to that of the atmosphere, it will possess energy owing to its motion, and so it will continue to flow out of the flask until this kinetic energy has been used up in forcing some gas out against the atmospheric pressure, with the result that the pressure of the gas in the flask will be less than atmospheric. The excess pressure of the atmosphere will now set the gas flowing into the flask again, and when its pressure is once more atmospheric it will continue to flow into the flask owing to its inertia until the kinetic energy is used up in producing an excess pressure in the flask. This cycle will now continue to repeat itself until all the kinetic energy of the gas has been dissipated as work done against frictional resistances. Now, since the tap C is closed quickly in the actual experiment, we have no means of knowing at what stage in the oscillations it is closed, and so we do not know the precise value of the pressure of the gas at the end of the adiabatic expansion. In general, it will not be atmospheric, which is what we have taken it to be in our results. The inconsistency obtained in the results obviously arises from this cause, but it has been overcome by Lummer and Pringsheim and later by Partington by applying the principle of the method directly, that is, by measuring the drop in temperature accompanying the adiabatic expansion.

128. Partington's Method.—Partington first designed a **bolometer** which would follow very rapid and small changes of temperature. It consisted of a platinum strip B of large area and very small thermal capacity which formed

one of the resistances of a Wheatstone's bridge. The galvanometer G must also be capable of registering very quick and small changes of current, and Partington selected for this purpose an Einthoven string galvanometer, which had a very small periodic time and would reach its steady deflection in 0.01 sec. If the air in the flask A was cooled (Fig 86), the resistance of the strip B decreased, the balance of the bridge was upset and the galvanometer registered a deflection in one direction; if the air was heated, the deflection was in the other direction. With this bolometer Partington was able to follow the rapid changes of temperature due to the oscillation which occurs when the flask is opened to the atmosphere, and succeeded in finding such

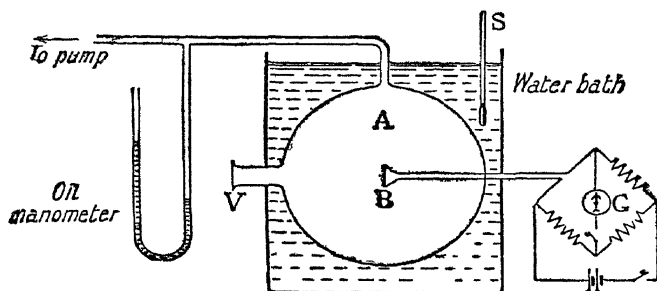


FIG 86.

an aperture for the valve V that no oscillations occurred, the pressure falling rapidly to that of the atmosphere. If the aperture was larger than the critical value, oscillation occurred, whereas if it was smaller, the decrease in pressure was too slow to be adiabatic.

The procedure in the actual experiments was as follows. The gas under test was pumped into the large flask A of 136 litres capacity, and its temperature was read from the standardised thermometer S when it has reached that of the water-bath, the corresponding pressure being read on the oil manometer. The balance of the bridge was then set to correspond to a lower temperature than that of the air, and the valve V was opened and left open.

As soon as the expansion was over, the balance of the bridge was tested and the experiment was repeated until such an initial pressure was obtained that the bridge was balanced immediately after the adiabatic expansion. The corresponding temperature was obtained by adding ice to the water-bath, which was well stirred the whole time, until the bridge was permanently balanced, showing that the air was at the temperature of the water-bath. The temperature was then read from the thermometer S. The corresponding pressure, which was that of the atmosphere, was read from a Fortin barometer. If p_1 and p_0 were the initial and final pressures respectively, and T_1 and T_0 were the corresponding absolute temperatures, γ was calculated from the equation (68)

This is probably the most accurate method of finding the ratio of the two specific heats of a gas, because the expansion is more nearly adiabatic than in any other experiment. In the first place, it is only the expansion of the air in the immediate neighbourhood of the bolometer which must be adiabatic, and so the remaining large volume of air merely serves as additional heat insulation. Secondly, any conduction of heat up the bolometer leads to the gas was compensated out.

129. The Ratio of the Adiabatic and Isothermal Elasticities of a Substance.—We shall now proceed to the derivation of an interesting relation between the two elasticities of *any substance*, which will enable us to find the equation to an adiabatic of an ideal gas in another way and also lead to yet another method of finding γ .

The elasticity of a substance is defined as

$$\text{Limit}_{\text{Stress} \rightarrow 0} \left(\frac{\text{Stress}}{\text{Strain}} \right).$$

It is necessary to take the limiting value of the ratio, since the stress is not in general proportional to the strain after the elastic limit is exceeded, and so the value of the ratio would depend on the magnitude of the increase in stress chosen, which is useless for the definition of a constant. We are concerned here with the bulk modulus of elasticity, E , the only modulus applicable to liquids and gases on

account of their having no shape. This is given by the expression

$$E = \frac{dp}{-\frac{dv}{v}} \quad \text{or} \quad E = -v \frac{dp}{dv},$$

where dp is the increase in pressure on the substance, $-dv$ is the corresponding decrease in volume, and v is the original volume. It is evident that the change in volume can take place under isothermal or adiabatic conditions and that it will be different in the two cases for a given increase in pressure. Consequently there will be two elasticities, the adiabatic and the isothermal elasticity, which we shall denote by the letters E_ϕ and E_θ respectively.

We shall now calculate the ratio of these two elasticities,

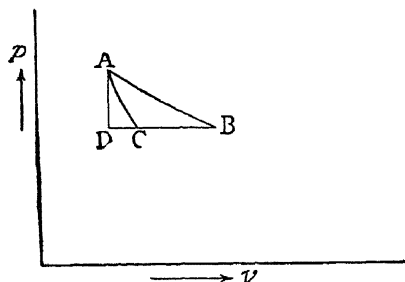


FIG. 87.

starting merely from the above definition. Let us suppose that we have unit mass of the substance in the condition represented by the point A in Fig. 87. Let the substance suffer an *infinitely small* isothermal expansion, represented by the curve AB, and let AC represent an *infinitely small* adiabatic expansion. AD is an *infinitely small* part of the constant volume line through A, and DB is an *infinitely small* portion of the constant pressure line through B. From the definition of bulk modulus of elasticity,

$$\frac{E_\phi}{E_\theta} = \frac{v_A \frac{AD}{DC}}{\frac{AD}{DB}} = \frac{DB}{DC},$$

v_A being the volume corresponding to the point A on the indicator diagram. Since the increases in volume DB and DC are infinitely small and take place at constant pressure,

$$\begin{aligned} \frac{DB}{DC} &= \frac{\text{Heat absorbed when the substance expands from D to B}}{\text{Heat absorbed when the substance expands from D to C}} \\ &= \frac{C_p dT}{\text{Heat absorbed when the substance expands from D to C}} \end{aligned}$$

dT being the difference in the temperatures corresponding to the points D and B

Now the work done in taking the substance round the cycle DACD is equal to the area enclosed by the cycle, which is nothing, in the limit, since DC and AD are of the first order of small quantities and therefore their product is of the second order and is equal to zero, in the limit. But we showed in Art 124 that the net amount of heat absorbed in a cyclical operation is equal to the external work done. So, in this case, the net amount of heat absorbed in taking the substance round the cycle DCAD is zero. Therefore the heat absorbed in taking the substance round the cycle DCAD is zero. Therefore the heat absorbed in taking the substance from D to C is equal to that given out in taking it from A to D, since there is no heat exchange along AC **as it is an adiabetic**. Therefore the heat absorbed in going from D to C is equal to that absorbed in going from D to A, which is $C_v dT$, the difference in temperatures corresponding to A and D being equal to those corresponding to D and B **since AB is an isothermal**. Careful attention should be paid to the two places in the argument at which we bring in the fact that one change is adiabatic and the other isothermal

$$\begin{aligned} \therefore \frac{DB}{DC} &= \frac{C_p}{C_v} \frac{dT}{dT} = \frac{C_p}{C_v}, \\ \therefore \frac{E_p}{E_v} &= \frac{C_p}{C_v} = \gamma. \end{aligned} \quad (70)$$

So we have the striking result that the ratio of the two elasticities of *any substance* is equal to the ratio of their specific heats. Our proof is valid for any substance since we have made no assumption as to the shape of the isothermal and adiabatic, except that the latter is the steeper, which we have previously shown to be true for all substances (Art 125)

130. An Alternative Method for the Equation to an Adiabatic of an Ideal Gas.—The equation to an isothermal of an ideal gas is

$$pv = \text{constant.}$$

Differentiating this, we have

$$p \cdot dv + v \cdot dp = 0,$$

$$\therefore -v \left(\frac{dp}{dv} \right)_\theta = p,$$

$$\therefore E_\theta = p.$$

From equation (70),

$$E_\phi = \gamma p,$$

$$\therefore -v \left(\frac{dp}{dv} \right)_\phi = \gamma p,$$

$$\therefore \frac{dp}{p} + \gamma \frac{dv}{v} = 0,$$

which is the same differential equation as we obtained when deriving the equation to an adiabatic by the First Law of Thermodynamics in Art 126. It integrates, as before, to

$$pv^\gamma = \text{constant.}$$

131. The Determination of γ from the Velocity of Sound.—Newton showed that the velocity of sound in a substance is given by

$$U = \sqrt{\frac{\bar{E}}{\rho}},$$

where U is the velocity of sound, E is the bulk modulus of elasticity of the substance, and ρ is its density. Newton thought that the compressions and rarefactions taking place at any point in a medium transmitting sound waves were isothermal, and so he used the isothermal elasticity in working out the velocity of sound in air from the above formula. His result came to 28,000 cm per sec compared with the experimental value of 33,000 cm per sec. It occurred to Laplace that the discrepancy was due to the fact that the compressions were adiabatic, and on substituting the adiabatic elasticity in the formula, he obtained good agreement with the experimental value. Rayleigh finally showed by another method that the adiabatic elasticity was

the correct one to use and so the expression for the velocity of sound in a gas becomes

$$U = \sqrt{\frac{\gamma p}{\rho}}.$$

If we measure U at known values of p and ρ , we can evidently calculate the value of γ for the gas. The standard text-books on Sound must be consulted for the various methods of measuring the velocity of sound in gases other than air. It is sufficient to say here that this method was used by Ramsay to determine the ratio of the specific heats of the rare gases, and that the results were sufficiently accurate to show that these gases were monatomic. We have already emphasised the importance of knowing the atomicity of the rare gases, as it leads to the only method of finding their atomic weights (Art 106).

EXAMPLES ON CHAPTER XII

1 Prove that the work done by a substance in expanding is $\int p \, dv$, and show how this may be represented on an indicator diagram

2 Discuss the importance of cyclical operations in the study of the laws governing the conversion of heat into work

3 Explain fully what is meant by an adiabatic change and show that, for any substance, a given decrease in pressure produces a greater increase in volume if the expansion is isothermal than if it is adiabatic, the initial pressure and volume being the same in each case

4 Explain what is meant by an adiabatic change. What effects are produced when (a) a dry gas, (b) a saturated vapour, expands adiabatically?

A volume of gas at 15°C expands adiabatically until its volume is doubled. Find the resultant temperature, given that the ratio of the specific heats of the gas is 1.4 (*Tripos*, Part 1)

5 Show how the fall in temperature due to the adiabatic expansion of a mass of gas may be calculated. If a cubic metre of air saturated with moisture at 20°C expands in rising in the atmosphere so as to increase its volume adiabatically in the ratio of 19 to 20, find its final temperature and the mass of water deposited. (Ratio of specific heats = 1.4, mass of

water vapour required for saturation of a cubic metre of air,
 10°C 9.33 grm, 12°C 10.57 grm, 14°C 11.96
 grm, 16°C 13.5 grm) (*Camb. Schol.*)

6 What is meant by an adiabatic transformation? Show that for such a transformation in a perfect gas $p\gamma v = \text{constant}$ where γ is the ratio of the specific heat at constant pressure to that at constant volume (*Oxford Schol.*)

7 Define an adiabatic change and derive the equation relating the pressure and volume of an ideal gas undergoing such a change

In a Wilson apparatus for photographing the tracks of α -particles the temperature of the air is 10°C . If its volume is increased in the ratio 1.375 : 1 by the expansion, assumed adiabatic, calculate the final temperature of the air. (The ratio of the specific heats of air = 1.41)

8 It is sometimes necessary to let the air out of a motor-car tyre in order to replace a faulty valve. If the air escapes so rapidly that its expansion may be considered adiabatic, calculate its temperature after it has escaped if it expands from a pressure of 35 lb per sq in to one 15 lb per sq in. The initial temperature of the air is 15°C .

9 A given mass of air and petrol vapour at 10°C is drawn into the cylinder of a motor car and its volume is decreased in the ratio of 5 : 1 by the compression stroke. If the decrease of volume is so rapid that it may be assumed adiabatic, calculate the final temperature of the mixture of air and petrol vapour. You may assume that the ratio of the specific heats of the mixture is 1.3.

10 What are isothermal and adiabatic lines on a p - v diagram?

A quantity of air at 0°C expands until its volume has increased by one-half. What is the final pressure if the expansion takes place (a) isothermally, (b) adiabatically, the equation to an adiabatic being $p\gamma v^{1.41} = \text{constant}$? Deduce the temperature after the adiabatic expansion, given that the coefficient of increase of pressure at constant volume is $\frac{1}{273}$ per $^{\circ}\text{C}$. (*Camb. Schol.*)

11 Describe Clément and Désormes' method of measuring the ratio of the specific heats of a gas at constant volume and constant pressure. (*Camb. Schol.*)

12 Discuss the disadvantages in Clément and Désormes' method of measuring the ratio of the specific heats of a gas, and show how they have been overcome in Partington's method.

13 How would you measure γ , the ratio of the two specific heats, for hydrogen? Discuss the significance of γ , and point

out in what ways a knowledge of its value is important (*Oxford Schol*)

14 Explain why a gas is said to possess two specific heats, and show the significance of their ratio γ

Describe carefully a method by which γ may be measured (*Camb Schol*)

15 Show that the adiabatic elasticity of a gas is equal to γp , where p is the pressure and γ the ratio of the specific heats of the gas

Outline the principal methods used in finding the velocity of sound in air (*Camb Schol*)

16 A gas expands under conditions which prevent heat from entering or leaving it. Discuss the two limiting cases

(a) very slow expansion,

(b) expansion into a region of low pressure, so that the external work done can be taken as negligible

Explain very briefly the bearing of (b) on the problem of producing low temperatures (*Trpos, Part I*)

17 Prove that the ratio of the adiabatic to the isothermal elasticity of any substance is equal to the ratio of its specific heat at constant pressure to that at constant volume. Show clearly why your result applies to any substance whatsoever

18 Show that in a gas the ratio of the velocity V of sound to the molecular velocity u is a constant which is independent of the pressure and the temperature. Find the value of this ratio for a monatomic gas,

$$V = \sqrt{\frac{E}{\rho}}$$

where E is the elasticity of the gas and ρ is the density (*Oxford Schol*)

CHAPTER XIII

THE SECOND LAW OF THERMODYNAMICS

132. Introductory.—We shall be concerned in this chapter with the physical principles underlying the operation of heat engines and refrigerators. We shall deal mainly with the purely scientific applications of these principles,

since they are almost of more importance and certainly of wider range than their engineering uses.

All heat engines and refrigerators are concerned with the transformation of heat into work, or vice-versa, and they must therefore obey the First Law of Thermodynamics. We have now to consider whether there is any further law governing their behaviour. It must be emphasised that this problem is solved by the usual scientific method of establishing the facts in connection with heat engines and refrigerators and then trying to induce some law from them. That this is so is borne out by the history of the development of the subject, for James Watt invented the steam engine in 1765, while a still more rudimentary form was produced by Newcomen as early as 1705, but the Second Law of Thermodynamics, which governs the behaviour of all heat engines, was not enunciated by Kelvin and Clausius until the middle of the nineteenth century. We shall accordingly commence with a short account of the heat engine and the refrigerator. We shall then be in a position to consider the physical principles common to all these machines.

133. Heat Engines.—As we are not concerned with the practical side of heat engines, but rather the physical principles common to them all, we shall not enter into the details of their construction, but shall confine ourselves to the points essential to each of them. Taking first the steam engine, a merely superficial acquaintance tells us that the essentials are the furnace, or **hot body** as we shall call it, the steam or **working substance**, and a condenser or **cold body**, which is the atmosphere in the case of locomotives, to which heat is rejected. The steam absorbs heat from the furnace, converts some of it into work by its expansive force applied to the piston, and rejects the rest to the condenser, as was shown by Hirn's experiments (Art 82). The essential point about this engine is the existence of the furnace at a higher temperature than the condenser; in other words, the conversion of heat into work only seems possible if the working substance falls in temperature.

Precisely the same principles are exemplified in the steam turbine, in which steam is raised to a high temperature by

a furnace and enters the system of blades, which it drives round by executing an adiabatic expansion, and then leaves the blades to enter a condenser at a lower temperature, to which it rejects that heat which it has been unable to convert into work. Again we have the furnace at a higher temperature than the condenser, again we only succeed in converting heat into work if the working substance suffers a drop in temperature.

Finally we see that the same thing is true of the internal combustion engine, which is used in motor cars and aeroplanes. Here the heat produced by the explosion of a mixture of air and petrol vapour constitutes the furnace and the atmosphere is once more the condenser, the air being the working substance. Here again we see that a source of heat at a higher temperature than the atmosphere is essential. Before trying to induce some general principle from the vast engineering experience which we have summarised, we must make one point quite clear. By a heat engine we mean a machine for producing a continuous supply of work. Work can be obtained from a given mass of air contained in a cylinder by cooling it to the absolute zero, but the process will not be continuous as it comes to an end then. A heat engine generates a continuous supply of work because it is cyclical, in the sense that the working substance is taken through a cycle of operations which can be repeated indefinitely. In this way we restore the working substance to its original condition, and so do not draw on its finite amount of internal energy. The source of energy, on the contrary, is the **hot body**. In practice it is not necessarily the same mass of working substance which is taken round the cycle again and again, but the principle of the engine is the same as if this were so. The only reason it is not done is because of its inconvenience.

We may sum up the essential features of all heat engines as found by practical experience in the following way. A heat engine must contain a hot body, which can supply heat at a high temperature, a cold body, to which heat may be rejected at a lower temperature, and a working substance, which can absorb heat from the hot body, convert some of it into external work by its expansion, and reject the rest to the cold body. The conversion of heat into work always

involves a drop in temperature of the working substance ; a continuous supply of work has never yet been obtained from a single supply of heat. There is far more heat in the Atlantic Ocean than is needed to drive the *Mauretania* to New York, but no engineer has yet learned how to use it. He has always so far had to carry another supply of heat at a higher temperature on his ship. No one has yet derived work from heat without two sources of heat at different temperatures. It would appear that it is a law of Nature that it is impossible to do so.

134. The Refrigerator.—We have already described the Electrolux refrigerator in Chapter VI, and we shall now deal with the more usual type, of which the *Frigidaire* is an example, more particularly from the point of view of the energy transformations which take place. As we pointed out when describing the Electrolux, the purpose of a refrigerator is the artificial production of cold. The *Frigidaire* type operates essentially by means of a compressor, which is driven by an electric motor or some other convenient source of energy. The **refrigerant**, which is the name given to the working substance in this case, is usually ammonia, carbon dioxide, or sulphur dioxide in the liquid state. The important thing is to use a substance with a high latent heat of vaporisation. It is taken through the following series of changes. It starts as a cold liquid in the spiral tube immersed in the brine-bath, the piston of the compressor is raised, causing the vapour in the cylinder to drop in pressure (Fig. 88). As soon as it is lower than the saturation vapour pressure of the cold liquid in the brine-bath, the valve *P* opens and some of the liquid evaporates into the compressor until the piston has reached the top of the stroke. The liquid absorbs the latent heat required for this evaporation from the brine-bath and this is how the low temperature is produced and maintained. The piston now commences its downward stroke driven by an electric motor, and as soon as the pressure of the vapour reaches the saturation value of the cold liquid, a spring closes the valve *P* and prevents any vapour from reaching the spiral in the brine-bath and condensing there again. The pressure of the vapour is thus increased until it rises to the value corresponding to

saturation at the temperature of the hot-water bath. When it is a little higher than this, it forces the valve *Q* open and vapour now flows to the spiral tube immersed in the hot-water bath. It condenses there and gives up the latent heat which it had absorbed from the brine-bath. The pressure of the vapour from this hot liquid is higher than that above the cold liquid, and so the liquid completes the series of operations by expanding through the valve *V* back to the brine-bath once more.

A refrigerator is essentially a machine for conveying heat from one body to another at a higher temperature, and it is quite clear that any refrigerator designed on these lines will necessarily involve a supply of mechanical work

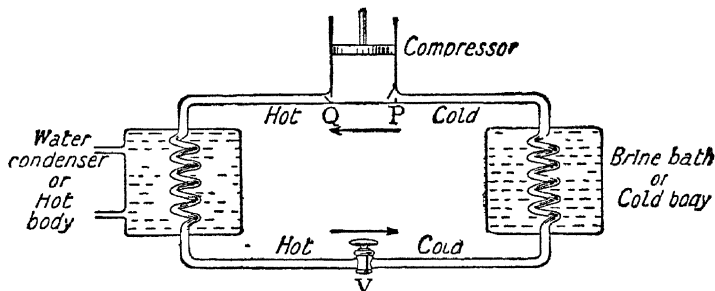


FIG 88

in order to force the vapour from the low pressure at the brine-bath to the high pressure at the water condenser. In other words, it is only possible to make heat go from cold to hot bodies by using up work. It will be realised that there is no question of a direct flow of heat, which can never take place up the temperature gradient. Considered from another point of view, the refrigerator may be considered as a heat engine working backwards. It has all the essentials of such an engine, but it absorbs heat from the cold body and uses up mechanical work which reappears as the increased amount of heat which it rejects to the hot body. We see that in the refrigerator the temperature difference between the hot and cold bodies is produced and maintained at the expense of mechanical work, whereas in

the heat engine mechanical work is produced by equalising the temperatures of the hot and cold bodies

The reader will remember that we described another type of refrigerator in Chapter VI. (Art 59), in which the evaporation of the refrigerant, liquid ammonia, was promoted by mixing it with an inert gas so as to reduce its partial pressure below saturation. The flow of the refrigerant was maintained by the application of heat so as to produce a convection current. We can see that this type of refrigerator is governed by the same fundamental principle as the Frigidaire; that it is necessary to supply energy in order to transfer heat from a cold to a hot body. In the case of the Electrolux, the energy is supplied in the form of heat.

135. The Second Law of Thermodynamics.—The facts and experience concerning heat engines and refrigerators were very much as we have described them in the foregoing articles, when Kelvin and Clausius made their celebrated statements of the Second Law of Thermodynamics, which governs the conversion of heat into work. This law, which could only have been a hypothesis, or guess, in the first place based on the knowledge of heat engines and refrigerators, has now become one of the most fundamental laws in the whole of physical science and, for reasons we shall outline later (Art 145), it is regarded as one which is known with a certainty greater than that of any other law.

We have seen that the fundamental fact about heat engines is that heat is extracted from a hot body, *some only* is converted into work and the rest *must* be given up to a cold body. It will be seen, therefore, that a heat engine works essentially by destroying the temperature difference which is essential to its operation. This leads to the first way of stating the Second Law of Thermodynamics due to Kelvin. “**It is impossible to derive a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings.**” It should be noticed that this law imposes a further restriction on the First Law of Thermodynamics. The first law merely requires that heat equivalent to the work done must come from somewhere, but either the hot or the cold body

will do. Then the second law steps in and rules out the cold body, just on the ground, in the first place, that no such heat engine has ever been produced.

We arrive at the second way of stating the second law from a consideration of the facts concerning refrigerators. We have seen that no one has ever produced a refrigerator which will work without a supply of energy. This is asserted to be essential in Clausius' statement of the second law according to which "**it is impossible to cause heat to pass from one body to another at a higher temperature without the aid of a supply of energy.**" It will be seen that these two generalisations are incapable of direct proof, since they are negative statements. Their justification is obtained in a way most common to nearly all the great scientific laws. The law is assumed to be true, and consequences of it are derived which lend themselves to accurate experimental test. The Second Law of Thermodynamics has been applied to a wider range of phenomena than any other single scientific law, it has been applied to change of state, to solution, to osmotic pressure, to the theory of the voltaic cell, to the rate of reversible chemical reactions, and last, and perhaps least, to the theory of heat engines. In every case both its qualitative and quantitative predictions have been verified by experiment. It is this accurate verification of consequences of the Second Law of Thermodynamics ranging over such a diversity of phenomena which constitutes its real justification. We shall deal with a few of these consequences later on in this chapter.

It should be realised that the two statements of the Second Law of Thermodynamics are equivalent to one another, they are merely different ways of saying the same thing and either can be derived from the other. Suppose, for example, that we have an engine which *does* give a continuous supply of work by cooling the cold body below the lowest temperature of its surroundings. This is a violation of the first statement of the second law. If the external work derived from the engine is used to drive a dynamo, which produces a current which generates heat in a coil immersed in the hot body, then we have produced a machine which causes heat to pass from one body to

another at a higher temperature without the expenditure of work. And this is a violation of the second way of stating the second law. The reader can easily show for himself that a violation of the second statement leads to that of the first.

136. The Carnot Engine.—We shall now continue our investigation into the laws governing the conversion of heat into work by considering an ideally simple heat engine, which is free from all the imperfections of actual engines and which, therefore, can be taken as the standard by which the performance of actual engines could be judged. The engine is called the Carnot engine, because it was first conceived by the French engineer, Sadi Carnot. His engine, which can never be realised in practice, consists of a hot

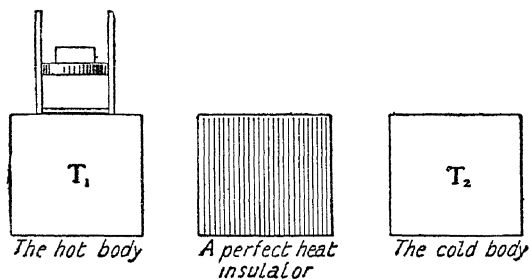


FIG 89.

body of infinite thermal capacity, a similar cold body, a perfect heat insulator, and a cylinder fitted with a piston enclosing a working substance which may be anything we please (Fig 89). The walls of the cylinder are also perfect heat insulators and the bottom is a perfect conductor. We do not, for the present, wish to specify the temperatures of the hot and cold body, but only to assure ourselves of their constancy, which can be done without having any scale of temperature or calibrated thermometer.

The working substance is taken through the following cycle of operations, known as the **Carnot cycle** (Fig 90). Starting at the condition represented by the point A, the cylinder is placed on the hot body and the load on the

piston is decreased so as to cause the force due to the pressure of the working substance to exceed that of the weight, and hence an expansion takes place. This expansion is strictly isothermal, since the bottom of the cylinder is a perfect conductor and the thermal capacity of the hot body is infinite. It is allowed to continue until the volume of the substance has reached that represented by the point B, when the cylinder is removed to the perfect heat insulator. An adiabatic expansion is now performed until the temperature of the working substance has fallen to that of the cold body, when the cylinder is removed to the cold body and the working substance is made to undergo an isothermal compression represented by CD. This is accomplished by keeping the weight on the piston just greater than the force due to the pressure of the working substance. When the point D is reached, the cylinder is put back on to the perfect heat insulator and the cycle is

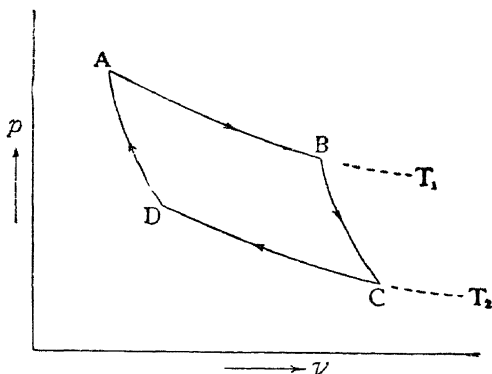


FIG 90.

completed by an adiabatic compression DA, which is stopped when the temperature of the working substance has risen to that of hot body once more. Sometimes objections are raised to starting the cycle at the point A on the grounds that it would be impossible to know when to stop the isothermal compression CD. The objection can easily be met by finding the volume corresponding to the point D by performing a preliminary adiabatic expansion of the working substance until its temperature had fallen to that of the cold body. If H_1 is the heat absorbed by the working substance from the hot body in the isothermal expansion AB and H_2 is the heat rejected to the cold body and W is

the external work done by the engine in one cycle, then

$$W = H_1 - H_2 \quad . \quad . \quad . \quad (71)$$

by the first law of thermodynamics. The **efficiency** E of a heat engine is defined as the ratio of the external work done in one cycle to the corresponding amount of heat absorbed from the hot body. In this case, then, we have

$$E = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1}.$$

$$\therefore E = 1 - \frac{H_2}{H_1} \quad . \quad . \quad . \quad (72)$$

137. Reversibility.—We have now to consider why the Carnot engine can be taken as the standard by which other engines are to be judged. It has two features which entitle it to this place. The first is this. We have seen that heat can only be converted into work if there are two sources of heat at different temperatures and that no work can be obtained from two sources of heat at the same temperature. It follows that the greater the temperature difference between the hot and cold bodies, the greater the efficiency of a heat engine. Now in many actual heat engines, all the heat is not absorbed at the temperature of the hot body, the working substance getting progressively colder as it absorbs heat, since it is doing work faster than it is absorbing heat. A similar thing may be true of the rejection of heat to the cold body. Such an engine is less efficient than the corresponding Carnot engine, since it does not make full use of the available temperature difference. But the Carnot engine does do so, since it takes in all its heat at one temperature, that of the hot body, and rejects its heat at one temperature, that of the cold body. Thus it is the ideal in this respect.

The second feature is that the Carnot engine is **reversible**. We shall now consider what **reversibility** is, what it implies, and how it can be realised. A reversible change is one which can be reversed by an infinitely small change in the value of the factors controlling it. It is one in which the opposing forces are infinitely close to equilibrium and therefore takes place infinitely slowly.

A reversible cycle is one which consists entirely of reversible changes and the cycle as a whole can therefore be performed in the opposite direction

What does a reversible change imply? We can see this most clearly by considering some cases of reversible and irreversible changes. We will consider in the first place the raising of a weight by the expansion of a gas in a cylinder in contact with the hot body of Carnot's engine. Let us suppose that there is friction between the piston and the walls of the cylinder. Then the force of the gas is greater than the weight to be raised by a finite amount equal to the force of friction. So the expansion is irreversible, since a finite increase in the weight is necessary to change it into a compression. We also see that the work done by the gas in a given increase in volume is less than that done on the weight by the work done against friction, whereas in the compression necessary to bring the gas back to its original condition, the precise opposite is the case. So the working substance can only be restored to its original condition by the expenditure of a finite amount of work, which means that an irreversible change implies a waste of energy, a transformation of heat into some form other than that of external work. In this case it is work done against friction. The energy is not lost, but it is none the less wasted. But if the piston is frictionless, the expansion is obviously reversible, and if the working substance is restored to its original condition, no expenditure of work is needed, since the work done on the weight during the expansion is just that needed for the necessary compression. So we see that, in a reversible change, a reversal of the direction of the change produces a reversal of the accompanying energy transformations. This reversal is precise and exact. In fact, a reversible change implies that there is no waste of energy; it ensures that any energy transformed is directed into the desired channel of external work.

We can also see that a finite temperature difference between the gas and the hot body involves irreversibility. Let us suppose that ACB (Fig. 91) represents the reversible isothermal expansion of the gas when the bottom of the cylinder is a perfect conductor, while ADB represents the corresponding expansion when the bottom of the cylinder

is of finite conductivity. It is evident that the expansion can only be reversed by taking the substance back along the path BEA, which means raising its temperature by a finite amount. Also the cycle ADBEA is irreversible in the sense that it cannot be performed in the opposite direction. So the expansion ADB is irreversible and it involves a waste of energy, since a finite amount of work equal to the area ADBEA must be done to restore the gas to its original condition. It is true that this work is converted into heat, but since the whole object of the machine is the reverse process, this decreases its efficiency. We see, then, that the whole point of a reversible change is that, when its direction is reversed, the energy transformations

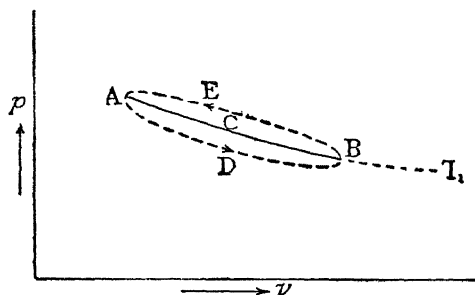


FIG 91.

are also reversed and so there is no waste of energy in such a change.

We have seen that the Carnot cycle is the most efficient cycle since the absorption and rejection of heat takes place at constant temperature, and it is now clear

that if the cycle is also reversible, any transformation of energy into other than the desired channel of external work is avoided, and therefore a Carnot reversible engine is obviously the standard by which to judge the performance of actual heat engines. How is reversibility to be realised? It cannot be done in practice, of course, but it is necessary to assure ourselves that it is feasible. All that is necessary is to have a frictionless piston and to maintain the gas at the same temperature as the body with which it is in contact by making the piston and the walls of the cylinder of perfect heat insulators and the bottom of the cylinder of a perfect conductor. In addition, the external force must never differ by more than an infinitesimal amount from that due to the working substance, which means that the changes take place infinitely slowly.

138. The Efficiency of all Reversible Engines Working between the same two Temperatures is the same — We shall now proceed to a very striking consequence of the second law of thermodynamics, which is of very wide application. It states that the efficiency of all reversible engines working on a Carnot cycle between the same two temperatures is the same. We shall demonstrate its truth by the method of *reductio ad absurdum*, which consists in assuming the proposition to be false, and showing that this leads to a conclusion which is contrary to established laws.

Let us suppose that we have an engine M which is more efficient than a Carnot reversible engine R working between the same two temperatures. We arrange that M shall work as a normal heat engine and drive R backwards. This means that R acts as a refrigerator, absorbing heat from the cold body, having work done on it, and rejecting both the heat and the work as heat to the hot body. Further we so arrange matters that M and R use the same hot and cold bodies, and that M absorbs in each cycle the same quantity of heat H from the hot body as R returns to it in working backwards. Now suppose M produces W_1 units of work and rejects $(H - W_1)$ units of heat to the cold body in each cycle. To work R backwards it must be supplied with W_2 units of work, and this together with $(H - W_2)$ units of heat absorbed from the cold body enables it to restore $(H - W_2) + W_2 = H$ units of heat to the hot body in each cycle as arranged. But since M is more efficient than R, W_1 is greater than W_2 , and so the combination of M and R produces a continuous supply of work, which can only come from the cold body. We see, in fact, that the cold body loses $(H - W_2) - (H - W_1) = (W_1 - W_2)$ units of heat in each cycle, which is just equal to the external work done. Sooner or later the cold body will reach a temperature lower than that of the coldest of its surroundings. But it is contrary to the second law of thermodynamics to produce a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings; therefore our initial assumption is untrue. That is, it is impossible to have an engine working between two temperatures more efficient than a Carnot reversible

engine working between the same two temperatures. From this it follows at once that the efficiency of all reversible Carnot engines working between the same two temperatures is the same.

We must now show that the efficiency of a reversible engine working on a Carnot cycle between two given temperatures is independent of the amount of heat absorbed from the hot body. If H is the heat absorbed in the cycle $AEFD$ (Fig. 92) and W , equal to the area $AEFD$, is the external work done, then the efficiency is $\frac{W}{H}$. Let the cycle $EBCF$ be such that the engine works between the same two temperatures as before and that

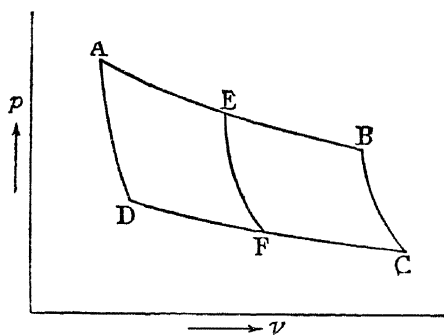


FIG. 92.

the heat absorbed is again H . Then the external work done is again W , since the efficiency is constant for a given quantity of heat absorbed and two given temperatures. Thus the area $EBCF$ is equal to W . Now consider the cycle $ABCD$. The heat absorbed is $2H$ and the external work done is equal to the

area $ABCD$, which is $2W$. Therefore the efficiency is $\frac{2W}{2H}$

or $\frac{W}{H}$, which is the same as before. Thus the efficiency of a reversible engine working on a Carnot cycle between two given temperatures is independent of the quantity of heat absorbed. Therefore the efficiency of a Carnot reversible engine depends only on the temperature of the hot and cold bodies and on nothing else.

The implication of this result is apt to be missed unless we stop to consider it for a moment. Provided the engine is reversible and is working on a Carnot cycle between

two given temperatures, its efficiency is entirely independent of the nature of the working substance, of the mechanism by which it takes up and rejects its heat, and of the way in which the external work is performed. Any property of matter in which heat can be converted into work can be used in the engine, provided that it is reversible. The working substance may be water, which absorbs its heat by changing into steam, whose expansive force does the external work; or the engine may use the expansive force of hot air, or it may depend on the Peltier conversion of heat into electrical energy, which can then be imagined to be converted into work by a motor. And all these diverse types of engine, some practical and others very unpractical but of the greatest theoretical importance, have the same efficiency. It is not surprising that the second law of thermodynamics is of such great importance when it leads to a consequence which is capable of such widespread and diverse applications.

The reader should also show for himself that the above proposition can be proved by arranging for M to supply just the amount of work needed to drive R backwards.

139. The Work Scale of Temperature.—When we were investigating the measurement of temperature, we found that all scales depending on the properties of a particular substance were arbitrary and disagree with one another to an extent which becomes really serious at high temperatures. We therefore decided to search for a scale which was independent of the properties of any one material substance both to meet this practical problem, but more particularly to satisfy an æsthetic desire for the "perfect" temperature scale. We saw that the ideal gas scale was in some measure satisfactory, in that it depends on the properties common to gases as a whole rather than on those of one gas. So far in our study of the diverse phenomena of heat we have not come across anything suitable for a non-arbitrary scale of temperature. But Lord Kelvin quickly seized on the result proved in the previous article for this purpose. It is evident that it has possibilities, for we are dealing with a quantity, the efficiency of a heat engine, which depends only on two temperatures and is entirely independent of the properties of

any particular substance Re-writing equation (72), we have

$$E = 1 - \frac{H_2}{H_1}$$

Let θ_1 and θ_2 be the temperature of the hot and cold bodies respectively on the new scale Then

$$E = k \phi(\theta_1, \theta_2),$$

where k is a constant and $\phi(\theta_1, \theta_2)$ is a function of the temperatures θ_1 and θ_2 of the hot and cold bodies respectively, and is entirely independent of the particular material substances used in the engine.

$$\therefore 1 - \frac{H_2}{H_1} = k\phi(\theta_1, \theta_2),$$

$$\therefore \frac{H_2}{H_1} = f(\theta_1, \theta_2), \text{ where } f(\theta_1, \theta_2) = 1 - k \phi(\theta_1, \theta_2).$$

Now Lord Kelvin *defined* this new scale of temperature by postulating that the function of the temperatures is to be equal to the argument In other words, temperature on the new scale is *defined* by the following equation :

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \quad . \quad . \quad . \quad . \quad (73)$$

It is evident that this scale is independent of the properties of any particular substance and is therefore quite non-arbitrary We shall call it the **work scale of temperature**, since it is based on the laws governing the conversion of heat into work

Before proceeding further we must satisfy ourselves that this definition of a scale of temperature is consistent with the behaviour of Carnot engines Suppose we have two engines A and B, of which A works between temperatures θ_1 and θ_2 and B between θ_2 and θ_3 If we arrange that A absorbs an amount of heat H_1 from the hot body and rejects H_2 to the cold body, while B absorbs H_2 and rejects H_3 , we have

$$\begin{aligned} H_1/H_2 &= \theta_1/\theta_2, \\ H_2/H_3 &= \theta_2/\theta_3. \end{aligned}$$

Merely from the mathematical form of these expressions, which follows from the definition of the work scale of temperature, we have by multiplication,

$$\frac{H_1}{H_3} = \frac{\theta_1}{\theta_3}.$$

But if we have a third engine C working between temperatures θ_1 and θ_3 and absorbing H'_1 and rejecting H'_3 , we have

$$\frac{H'_1}{H'_3} = \frac{\theta_1}{\theta_3}.$$

If we make $H'_1 = H_1$, then $H'_3 = H_3$. In other words, if C absorbs the same amount of heat from its hot body as A does from its hot body, then C must reject the same amount of heat to the cold body as B does. Is this true of Carnot engines? It can be seen that it is by supposing that the cold body of A is also the hot body of B. It is then evident that A and B working together are equivalent to C.

We must now consider the second stage in the realisation of the "perfect" scale of temperature, namely, its practical realisation. This raises serious difficulties; in its simplest form, it involves the construction of a Carnot engine and the measurement of the heats absorbed and rejected. From this the ratio of the temperatures of the hot and cold bodies on the work scale could be calculated, and if their temperatures are also measured by a thermometer calibrated on, say, the constant volume hydrogen scale, the relation between this scale and the work scale can be investigated. Unfortunately we cannot even begin to do this, since we cannot make a Carnot engine, reversibility lies outside practical possibility. We must try, then, if we can calculate the heats absorbed and rejected theoretically by using as the working substance something whose properties are known from experiment in terms of a practical scale of temperature, such as the constant volume hydrogen scale. We can hope in this way to find the relation between this scale and the work scale. One thing that is hopeful here is that we are free to choose any working substance we please, since the efficiency of the engine is

the same for all. It was at the suggestion of Joule that Lord Kelvin turned his attention to the ideal gas scale, and he succeeded in correlating this scale with the work scale by using the ideal gas as the working substance in a Carnot engine.

140. The Relation between the Ideal Gas Scale and the Work Scale.—Let us suppose that we have a Carnot engine using unit mass of an ideal gas as the working substance and that we take it round the usual Carnot cycle

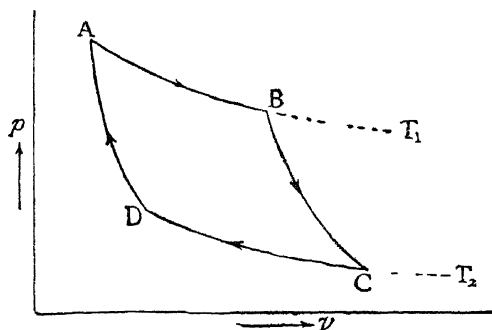


FIG 93.

ABCD (Fig 93). Let the temperature of the hot and cold bodies be T_1 and T_2 respectively on the ideal gas scale and θ_1 and θ_2 on the work scale, and let p_a and v_a be the pressure and volume respectively corresponding to the point A, the same letters

with the corresponding subscripts being used to denote these quantities at B, C, and D. If H_1 is the heat absorbed from the hot body during the isothermal change AB and H_2 is the heat given up to the cold body during the isothermal compression CD, we have, by definition of the work scale of temperature,

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \quad . \quad . \quad . \quad (73)$$

We now proceed to calculate H_1 and H_2 in terms of T_1 and T_2 from the known properties of the ideal gas. Applying the first law of thermodynamics to the change AB, we have $H_1 =$ (the increase in internal energy of the gas in going from A to B) + (the external work done by the gas). But since the gas is an ideal gas, its internal energy depends only on the temperature, and as AB is an isothermal change, there is no change in internal energy in going from A to B.

$\therefore H_1$ = the external work done by the gas in going from A to B

$$= \int_{v_a}^{v_b} p \, dv = rT_1 \int_{v_a}^{v_b} \frac{dv}{v} = rT_1 \left[\log_e v \right]_{v_a}^{v_b},$$

$$\therefore H_1 = rT_1 \log_e \frac{v_b}{v_a} \quad . \quad . \quad . \quad (74)$$

Similarly, H_2 = (the external work done on the gas in going from C to D)

$$= \int_{v_d}^{v_c} p \, dv = rT_2 \int_{v_d}^{v_c} \frac{dv}{v} = rT_2 \left[\log_e v \right]_{v_d}^{v_c},$$

$$\therefore H_2 = rT_2 \log_e \frac{v_c}{v_d} \quad . \quad . \quad . \quad (75)$$

Dividing (74) by (75), we have

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \frac{\log_e \frac{v_b}{v_a}}{\log_e \frac{v_c}{v_d}} \quad . \quad . \quad . \quad (76)$$

We must now introduce into our reasoning the fact that we are using a Carnot cycle, that is, the fact that AB and CD are isothermals and AD and BC are adiabatics. This leads to the following four equations, from which we can eliminate p_a , p_b , p_c , and p_d and find a relation between v_a , v_b , v_c , and v_d

$$\begin{aligned} p_a v_a &= p_b v_b \\ p_a v_a &= p_c v_c \\ p_a v_a^\gamma &= p_d v_d^\gamma \\ p_b v_b^\gamma &= p_c v_c^\gamma \end{aligned}$$

Dividing the third of these equations by the fourth, we have

$$\frac{p_a}{p_b} \cdot \left(\frac{v_a}{v_b} \right)^\gamma = \frac{p_d}{p_c} \cdot \left(\frac{v_d}{v_c} \right)^\gamma.$$

From the first of these equations $\frac{p_a}{p_b} = \frac{v_b}{v_a}$,

and from the second $\frac{p_d}{p_c} = \frac{v_c}{v_d}$.

Substituting the values of these ratios in the fifth equation, we have

$$\begin{aligned}\frac{v_b}{v_a} \left(\frac{v_a}{v_b}\right)^\gamma &= \frac{v_c}{v_d} \left(\frac{v_d}{v_c}\right)^\gamma, \\ \therefore \left(\frac{v_a}{v_b}\right)^{\gamma-1} &= \left(\frac{v_d}{v_c}\right)^{\gamma-1}, \\ \therefore \frac{v_b}{v_a} &= \frac{v_c}{v_d} \quad . \quad . \quad . \quad . \quad (77)\end{aligned}$$

Substituting equation (77) in equation (76), we have

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \quad . \quad . \quad . \quad . \quad (78)$$

Comparing equation (73) and (78), we have

$$\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2} \quad . \quad . \quad . \quad . \quad (79)$$

Let us now consider the interpretation of this result. If $T_1 = 0, \theta_1 = 0$; that is, the two scales have the same zero. If we further arrange for them to have the same size of unit by postulating that there shall be 100 degrees between the lower and upper fixed points on the work scale as there are on the ideal gas scale, then

$$\frac{T_0}{T_0 + 100} = \frac{\theta_0}{\theta_0 + 100},$$

where T_0 and θ_0 are the temperatures of the lower fixed point on the ideal gas scale and work scale respectively. Therefore $T_0 = \theta_0$, that is, the temperature at which pure ice melts at 1 standard atmosphere is the same on the two scales. Finally, if T and θ are the temperature of any body on the two scales,

$$\frac{T_0}{T} = \frac{\theta_0}{\theta}.$$

But $T_0 = \theta_0$; $\therefore T = \theta$; that is, any temperature is the same on the two scales, *which are therefore identical*.

There is still a third stage in the practical realisation of the work scale which cannot be treated fully in this book but which must be mentioned. The ideal gas scale cannot be realised directly, since actual gases only tend

to the ideal gas at very low pressures. Nevertheless, it is possible to calculate from a temperature measured on, say, the constant volume hydrogen scale the corresponding temperature on the ideal gas scale. This is done by using the measured deviations of hydrogen from the ideal gas obtained from the porous plug experiment, but more advanced books on heat must be consulted for a full treatment of the calculation. So we have now brought to a successful conclusion one of the outstanding problems with which we were confronted at the very beginning of our study of heat; we have been able to conceive of a scale of temperature entirely satisfying to the æsthetic sense, we have designed a thermometer which will give the same reading when put in the same substance whatever it is made of. Further, we have found a way of realising such a thermometer in practice. And it cannot be too strongly emphasised that in satisfying our æsthetic sense, we have also solved an urgent practical problem in the measurement of temperature, for the disagreement between the different scales is a really serious matter at the very high temperatures at which the physicist is accustomed to work nowadays.

Before proceeding to some applications of the second law of thermodynamics, it is important to emphasise one point in the above proof of the identity of the work scale and the ideal gas scale, which often escapes attention. The ideal gas is that gas to which all actual gases tend at infinitely low pressure, it has a coefficient of expansion of $\frac{1}{273.20}$ per °C at 0° C and therefore the absolute temperature of the ideal gas scale of the lower fixed point is 273.20. This gas is a real physical substance, although it can never actually be realised. But what is there in the above proof of the identity of the work scale and the ideal gas scale which compels us to use the "physical" ideal gas? Why should we not use a "mathematical" ideal gas, which obeys the ideal gas equation, but has any coefficient of expansion at 0° C we like to imagine, say, $\frac{1}{100}$ per °C? All the equations from (72) to (78) are still true, and so the work scale agrees with a temperature scale, according to which the absolute temperature of the lower

fixed point is 100, or indeed anything we like according to our choice of the coefficient of expansion of the "mathematical" ideal gas. This is a ridiculous conclusion, and there is surely a flaw in the argument somewhere. The solution of the difficulty is that we have no right to use the "mathematical" ideal gas as the working substance in the Carnot engine. The ideal gas is used to get over the fact that it is impossible to measure H_1 and H_2 experimentally; we are justified in substituting this calculation for the measurement because the second law of thermodynamics asserts that the result of the calculation or the measurements, if we could make them, will be the same whatever the substance used. But the second law is a hypothesis based on experience with heat engines and refrigerators using actual substances. It is only valid, therefore, for actual substances, and so we must use the "physical" ideal gas as the working substance in the Carnot engine.

141. The Latent Heat Equation.—We shall now proceed to the application of the second law of thermodynamics to the phenomena of change of state, and we shall find that we are able to make certain qualitative and quantitative predictions. It is the accurate verification of such predictions, both in this and other fields, which constitutes the chief support for the second law of thermodynamics.

We commence by expressing both the first and second laws in a convenient mathematical form. Using the usual notation,

$$\begin{aligned} W &= H_1 - H_2, \\ \frac{H_1}{H_2} &= \frac{\theta_1}{\theta_2} \end{aligned}$$

are the two equations expressing the first and second laws respectively. The second equation may be re-written in the form

$$\frac{H_1 - H_2}{H_2} = \frac{\theta_1 - \theta_2}{\theta_1}.$$

Substituting the first equation in this, we have

$$\frac{W}{H_1} = \frac{\theta_1 - \theta_2}{\theta_1}$$

If the difference in temperatures between the hot and cold bodies is the infinitely small quantity $d\theta$, the work done in one cycle is dW , and the heat absorbed from the hot body at temperature θ is H , this equation becomes

$$\frac{dW}{H} = \frac{d\theta}{\theta} \quad . \quad . \quad . \quad (80)$$

This equation is the most convenient mathematical expression of the two laws of thermodynamics. We shall now apply it to the case of change of state from liquid to gas.

We shall suppose that we have a Carnot engine filled with unit mass of the liquid in the state represented by the point A (Fig 94) and that it is taken through the Carnot cycle ABCD. AB is the isothermal expansion caused by decreasing the external load on the piston to a value less than that of the saturation vapour pressure of the liquid at temperature θ . The liquid therefore commences to evaporate and continues

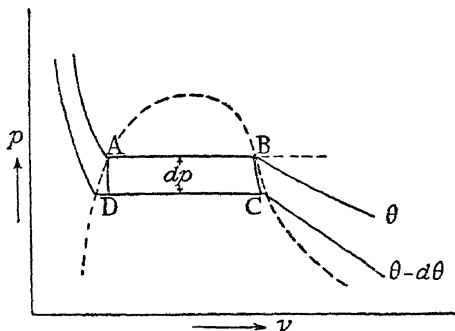


FIG 94

to do so until all of it has been converted into vapour, when it reaches the condition represented by the point B. The necessary latent heat L is absorbed from the hot body. This is followed by the adiabatic expansion BC , during which the vapour will not, in general, remain saturated. In the case of steam, for example, some of it will condense. The isothermal compression CD then takes place, and the cycle is concluded by the adiabatic compression DA . It should be emphasised that it is not only during the isothermal changes that changes of state occur, they will also happen during the adiabatic changes. *We are only justified in applying the laws of thermodynamics to this cycle if it is reversible.* A little consideration will show that this

is so, both in the sense that it can be performed in the opposite direction and that each change in it can be reversed by an infinitely small change in the load on the piston.

For the cycle ABCD we have

$$\begin{aligned} H &= L \\ \text{and} \quad dW &= (v_2 - v_1)dp, \end{aligned}$$

where v_2 and v_1 are volumes of unit mass of the saturated vapour and liquid respectively at temperature θ , in general v_2 is the volume of unit mass of the substance *after* it has absorbed the latent heat, and v_1 its volume before it has absorbed the latent heat, dp is the difference in saturated vapour pressure at temperatures θ and $\theta - d\theta$. Substituting these values in equation (80), we have

$$\begin{aligned} \frac{(v_2 - v_1)dp}{L} &= \frac{d\theta}{\theta}, \\ \therefore \frac{dp}{d\theta} &= \frac{L}{\theta(v_2 - v_1)}. \quad \cdot \quad \cdot \quad \cdot \quad (81) \end{aligned}$$

This is known as the latent heat equation, and it can be seen that it applies equally well to the change of state from solid to liquid, since we have assumed nothing in our reasoning which is not true of such change. We shall now apply the equation to the cases of water and steam and ice and water.

In the case of the change from water to steam, we know that v_2 is greater than v_1 . L and θ are necessarily positive, and so equation (81) predicts that the vapour pressure of water will increase with temperature, a prediction which is verified by experiment. It further enables us to calculate the rate of increase. For, from various experimental measurements, at $\theta = 373.20$, $L = 539.4$ cals per grm, $v_2 = 1677$ c.c., $v_1 = 1$ c.c., and $J = 4.186 \times 10^7$ ergs per calorie. Substituting these values in equation (81), we have

$$\begin{aligned} \frac{dp}{d\theta} &= \frac{539.4 \times 4.186 \times 10^7}{373.20 \times 167} \text{ dynes per sq. cm. per degree} \\ &= \frac{538.7 \times 4.186 \times 10^7 \times 760}{373.2 \times 1676 \times 1.013 \times 10^6} \text{ mms of mercury per degree,} \end{aligned}$$

since 1.013×10^6 dynes per sq cm equals one standard atmosphere or 760 mm of mercury.

$$\therefore \frac{dp}{d\theta} = 27.09 \text{ mm of mercury per degree at } 373.20^\circ \text{ A.}$$

or 100° C Holborn and Henning's experiments give 27.16 mm of mercury per degree at 100° C , and so the calculated and experimental values are in excellent agreement. Alternatively, as mentioned in Art 71, we can assume the truth of equation (81) and use it to calculate v_2 , the volume of 1 grm of saturated steam at 100° C . Using the above numbers, we obtain $v_2 = 1673 \text{ c.c.}$

Turning now to the case of ice and water, we know that v_2 is less than v_1 , for v_2 is the volume of the substance after it has absorbed the latent heat and ice contracts when it melts. As before L and θ are again positive, and so the latent heat equation predicts that $\frac{dp}{d\theta}$ is negative,

that is, the melting-point of ice decreases with pressure. It is easy to see that the converse is predicted of substances such as paraffin wax, which expand when they melt. Both of these predictions have been verified by experiment. Furthermore, the actual change in the melting point per atmosphere can be predicted. In the case of ice, we have at $0^\circ \text{ C. or } 273.20^\circ \text{ A.}$, $L = 79.7 \text{ cal. per grm.}$, $v_2 = 1.000 \text{ c.c.}$, $v_1 = 1.091 \text{ c.c.}$ Substituting these values in equation (81), we have

$$\begin{aligned} \frac{d\theta}{dp} &= \frac{273.2 (1.000 - 1.091)}{79.7 \times 4.186 \times 10^7} \text{ degrees per dyne per sq cm.} \\ &= - \frac{273.2 \times 0.091 \times 1.013 \times 10^6}{79.7 \times 4.186 \times 10^7} \text{ degrees per atmosphere} \\ &= - 0.0075 \text{ degrees per atmosphere} \end{aligned}$$

Dewar's experiments (Art 54) gave the result -0.0072 degrees per atmosphere, which is in good agreement with the predicted value.

142. Entropy.—We shall conclude this chapter with an account of another aspect of the second law of thermodynamics involving the introduction of a new quantity called **entropy**. It is rather a difficult conception, but it is nevertheless one of the most important quantities

in physics, as well as being extremely useful to the engineer in purely practical problems

In a Carnot reversible cycle, we know from the second law of thermodynamics, combined with the definition of the work scale of temperature, that

$$\frac{H_1}{\theta_1} = \frac{H_2}{\theta_2}$$

using the previous notation. But H_1 is heat absorbed and H_2 is heat emitted by the working substance, and so these should be given different signs to obtain the equation in strict mathematical form. Calling H_2 negative, the above equation becomes

$$\frac{H_1}{\theta_1} + \frac{H_2}{\theta_2} = 0 \text{ for the whole cycle.}$$

We define $\frac{H_1}{\theta_1}$, or the heat absorbed by a body divided by the temperature at which it is absorbed, as the increase in

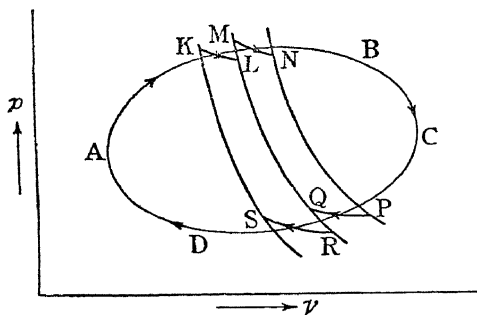


FIG 95

entropy of the body in passing from the initial to the final state. It must be emphasised that this statement is only true for reversible changes. The above equation shows that the increase in entropy of the working substance during the isothermal expansion added to the

increase during the isothermal compression is equal to nothing. In other words, the entropy of the working substance is the same at the end of the cycle as at the beginning.

We shall now show that this is true of any reversible cycle in which the temperature is continually varying by proving that such a cycle can be considered as made up of an infinite number of Carnot cycles, as shown in Fig 95.

The substance is taken round the reversible cycle ABCDA. Let KS, MR, NP represent a set of adiabatics and KL, MN, PQ, RS a set of isothermals. Consider the cycle A KLMN . PQRS A. There is no absorption of heat along the parts of the adiabatics traversed, and if dH_r is the heat absorbed along KL and dh_r is the heat absorbed along RS, we have

$$\frac{dH_r}{\Theta_r} + \frac{dh_r}{\theta_r} = 0,$$

since these two isothermals together with the adiabatics make up a Carnot cycle.

Summing up for all the isothermals constituting the main cycle, we have

$$\sum \left(\frac{dH_r}{\Theta_r} + \frac{dh_r}{\theta_r} \right) = 0,$$

or

$$\int \frac{dH}{\theta} = 0,$$

the integration being extended to all the isothermals in the cycle. But, as there is no absorption of heat along an adiabatic, this equation is true not only for the isothermals but also for the whole cycle A KLMN PQRS.

A. Now this cycle can be made to coincide as nearly as we like with the actual cycle ABCDA, through which the working substance is taken, by making KL_1MN . PQ_1RS . . sufficiently small. Therefore for the cycle ABCDA,

$$\int \frac{dH}{\theta} = 0,$$

the integration being taken round the cycle. Now, if a substance absorbs a quantity of heat dH at a temperature θ , its increase in entropy $d\phi$ is given by

$$d\phi = \frac{dH}{\theta} \quad . \quad . \quad . \quad (82)$$

Substituting this in the previous equation, we have

$$\int d\phi = 0 \quad . \quad . \quad . \quad (83)$$

for the whole cycle. That is, the entropy of the substance is the same at the end of the reversible cycle as at the beginning, or the change of entropy for the whole cycle is zero.

It follows immediately from this result that the entropy of a substance depends only on its condition, and is quite independent of the way in which it arrived at that condition. For let us suppose that a substance is taken from A to B via C and returned to A via D (Fig 96). Then (the change in entropy in going from A to B via C) + (the change in entropy in going from B to A via D) = 0 from equation (83).

∴ the change in entropy in going from A to B via C = the change in entropy in going from A to B via D

Therefore if ϕ_A and ϕ_B is the entropy of the substance at A and B respectively, $\phi_B - \phi_A$ is independent of the path taken and depends only on the points A and B. Thus the entropy of a substance depends only on its state, which, we have seen, is uniquely determined by any two quantities, such as its pressure and volume. Entropy, in fact, is like the internal

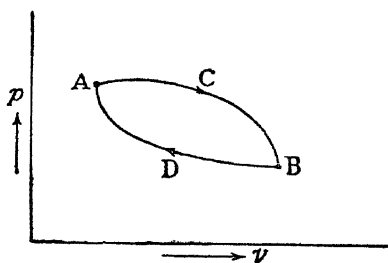


FIG 96

energy of the substance in this respect.

We may illustrate the difference between entropy and heat by considering the case of the Carnot cycle ABCD (Fig 93). The increase in entropy of the working substance in going from A to C via B is the same as the decrease in entropy in going back to A via D. But this is quite untrue of the heat absorbed, for the heat H_1 absorbed in going from A to C via B is greater than that H_2 given up in returning to A via D by an amount equal to the external work done. Unlike entropy, then, the heat absorbed by a substance in going from one condition to another does depend on the path by which the change takes place.

We can only measure difference in entropy, but, as with other quantities, such as height and electric potential, we choose an arbitrary zero for convenience, and in this way we can state the entropy of a substance. But it is really only the difference in entropy between the substance in its present state and that when it is in the standard state. A substance is said to have zero entropy when it is at 0°C and 760 mm pressure.

143. The Principle of the Increase in Entropy.—We shall now proceed to a proposition of great importance which is a consequence of the second law of thermodynamics. Let us suppose that the working substance in a Carnot engine absorbs reversibly a quantity of heat H from the hot body at temperature θ . Since the process is reversible, the temperature of the working substance is also θ during the absorption. Let us suppose that this absorption causes the substance to expand from a state A to a state B. Then the increase in entropy, $\phi_b - \phi_a$, of the working substance is given by

$$\phi_b - \phi_a = \frac{H}{\theta}$$

But this is also the decrease in entropy of the hot body. Therefore as a result of this *reversible* change, there is no change in entropy of the whole system, hot body and working substance.

But now let us suppose that the working substance expands between the same states as before, but *irreversibly* this time. Since the entropy of a substance depends only on its condition, the change in entropy of the working substance is the same as before, $\frac{H}{\theta}$. Now if we suppose the irreversibility is due to the bottom of the cylinder not being a perfect conductor, the temperature of the hot body is θ_1 , where $\theta_1 > \theta$. So the loss in entropy of the hot body = $\frac{H}{\theta_1}$ since only the same amount of heat has to be absorbed as in the reversible case

Since $\theta_1 > \theta, \frac{H}{\theta_1} < \frac{H}{\theta}.$

Therefore the gain in entropy of the working substance is greater than the loss of entropy of the hot body, that is, the system as a whole gains entropy in this irreversible change. The same result will be obtained if the working substance is giving heat to the hot body as the result of an isothermal compression, or if any other cause of irreversibility is considered.

These two results are particular cases of a general proposition that **the entropy of an isolated system either remains constant or increases according as the changes it undergoes are reversible or irreversible.** Stated mathematically,

$$d\phi > 0,$$

according as the change is irreversible or reversible. The proof of this proposition in its most general form is beyond the scope of this book, but can be found in Roberts' *Heat and Thermodynamics*. So we see that the necessary and sufficient condition of equilibrium of an isolated system is that the entropy should be a maximum, for then ϕ cannot increase and so $d\phi \nless 0$. When this condition is reached, no further change can occur, no further transformation of energy can take place; nothing more can happen. The system will be stagnant.

144. The Degradation of Energy.—The same result can be arrived at in a different way, which is very instructive. If a heat engine working between temperatures T_1 and T_2 absorbs a quantity of heat H_1 from the hot body, by the second law of thermodynamics it must reject a quantity H_2 to the cold body, where

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

The balance, $H_1 - H_2 = W$, is converted into work. Hence only W units of work out of the H_1 units of heat absorbed are "available" for conversion into useful work; the remainder must be rejected. W is called the amount of **available energy** produced by the system having a total energy H_1 . Now

$$\frac{W}{H_1} = \frac{H_1 - H_2}{H_1} = \frac{T_1 - T_2}{T_1},$$

$$\therefore W = \left(\frac{T_1 - T_2}{T_1} \right) H_1.$$

This gives the relation between the available energy and the total energy of the system. It shows very clearly that energy is only available in a useful form from heat if there are two supplies of heat at a different temperature, and that the greater the temperature difference, the greater the fraction of heat which can be converted into useful work, or the greater the availability of the energy.

When all the heat in the physical universe is at the same temperature, none of it can be converted into mechanical work, there will be as much energy present as there is now, but none of it will be of any use for the practical purposes of raising loads and producing movement. The physical universe will be stagnant! This state is inevitably being approached, since many factors are at work equalising temperature difference such as the operation of heat engines themselves and conduction. This is referred to as the **degradation of energy**, meaning that energy is assuming a form which makes it less useful to us. The universe is destined to die a "heat death!"

It will be seen that we have arrived at the same result as was reached in the previous article, which is applicable to the physical universe considered as an isolated system. We can easily see that the entropy of the universe is a maximum when all the heat is at the same temperature. For if h calories flow from a body at temperature T_1 to one at temperature T_2 , the gain in entropy of the universe $= \frac{h}{T_2} - \frac{h}{T_1}$, which is positive while $T_2 < T_1$. So the entropy cannot be a maximum while temperature differences persist.

145. The Statistical Aspect of the Second Law of Thermodynamics.—We shall conclude this chapter by considering a possible violation of the second law of thermodynamics, which will reveal its true nature and the reason for the great confidence with which its truth is asserted. Let us suppose that we have a chamber containing a gas divided into two halves A and B by a partition with a frictionless door. The gas in the two halves is assumed to be in thermal equilibrium, that is, its temperature and therefore the average velocity of its molecules is the same. But we saw in Chapter IX on

the kinetic theory of gases that the velocities of the individual molecules were distributed according to a definite law about this average, and so both in A and in B there will be molecules whose velocities are widely different from the corresponding average. Let us imagine that we can command the services of a "demon" who has the ability to follow the doings of individual molecules, and that we instruct him to open the door whenever a fast molecule is going from B to A or a slow one from A to B, and to close it whenever a slow one is going from B to A or a fast one from A to B. In this way we shall collect all the fast moving molecules in A and all the slow ones in B, that is, the temperature of A will become higher than that of B. In other words *we have produced a difference in temperature between two bodies originally at the same temperature without the expenditure of mechanical work*, for the door can be weightless and frictionless. This is contrary to the second law of thermodynamics. This example, which was first thought of by Maxwell, is important, not because it suggests a possible way of violating the law in practice, but because it ultimately leads to the conclusion that the second law of thermodynamics stands out as the most certain of all physical laws. For we can, as it were, lay odds against the second law being violated by working out mathematically the chance against the sorting accomplished by the demon occurring accidentally. The odds are enormous simply because in any practical case the number of molecules dealt with is of the order of 10^{24} . If the number of individuals were small, say of the order of 10, the chance against violation would be quite small, so small that in practice it would continually be occurring. This point is so important that it will be illustrated by another example in which the probabilities can easily be calculated.

Let us suppose that the same chamber as before is used, only that this time A is filled with gas and B is exhausted. If the two halves are put into communication, the gas expands irreversibly from A into B until the pressures are equal. This irreversible expansion is accompanied by an increase of entropy, and so it would be contrary to the second law of thermodynamics for the gas all to return to

A again, as this would involve a decrease in entropy. And the law of increase of entropy is a consequence of the second law of thermodynamics, and is regarded by some as the most convenient mathematical statement of the law. Now let us suppose that there are only two molecules in the gas originally in A. The probability of both those molecules being in A at the same time, after it has been put into communication with B is $\frac{1}{4}$ or $(\frac{1}{2})^2$. This follows from the fact that there are four possible distributions of the molecules between A and B, only one of which is the required distribution. So the chance against the second law being violated is 4 to 1, which is comparatively small. But if there are n molecules in the gas, the probability of all these molecules being in A at the same time is $(\frac{1}{2})^n$. If n is 10^{24} , a typical case, this is so improbable as to amount to impossibility in practice. So we see that the second law of thermodynamics is true, and so very certainly true, merely because we are dealing with systems consisting of very large numbers of individuals. It owes its validity solely to this fact, and that explains its wide range of applicability, for the law is a law which holds for any large number of individuals, whatever their nature. *It is, in fact, a statistical law.* It is definitely not true for systems consisting of a small number of individuals. And the reason for our certainty in its truth, for our saying that it stands out as the most firmly established of all laws in physical science, is that we can calculate the chance against its being violated and the odds are so overwhelming as to amount to certainty in practice. There is far less chance of the second law being violated than there is of a child who has never seen or touched a piano before playing a Bach fugue on the first occasion it idly runs its hands over the keys!

It is interesting to connect up entropy with this aspect of the second law of thermodynamics. Let us compare the perfectly elastic rebound of a rubber ball from the floor, in which it rises to its original height, with an inelastic rebound in which, for simplicity, we shall suppose all its kinetic energy is destroyed and converted into heat. When the ball strikes the ground, it has both kinetic energy and also organisation of that energy, in the sense that the

molecules all have a common energy of motion in the same direction as well as the random energy due to their heat. In the elastic rebound, which is reversible, both the energy and its organisation are preserved, for the velocity of all the molecules is exactly reversed in direction and unaltered in magnitude. But in the inelastic rebound, which is irreversible, the kinetic energy is preserved as heat, but its organisation is destroyed, for the direction of the motion is now different for different molecules. In the elastic rebound, entropy remains unchanged, in the inelastic case it increases. So we see that entropy corresponds to the lack of organisation in the individuals of the system, or to what Eddington calls the "random element," which remains constant for the elastic rebound and increases at the inelastic rebound. We now see the interpretation of the law of increase of entropy, for it merely means an increase in the random element of the system. This is an inevitable result of an interaction of the individuals, in the same way that the shuffling of a pack of cards increases their disorganisation or random element. And the chance of entropy decreasing is the same as that of the lack of arrangement of a pack of cards being decreased by shuffling, it is so small as to amount to practical impossibility since there are so many "cards" in the pack in the case of entropy. For a more comprehensive treatment of these ideas, the reader should consult *The Nature of the Physical World*, by Sir Arthur Eddington, from which the above treatment is taken.

To sum up, then, we divide the development of the second law of thermodynamics into three stages. The first stage is the statements of the law by Kelvin and Clausius, which were inductions or guesses based on the experience of heat engines and refrigerators. The second stage consists in the development of the consequences of the law to a wide range of phenomena and their confirmation by experiment in every case. And at the third stage comes the understanding of the statistical nature of the law derived from the properties common to all systems consisting of a large number of individuals of any kind. It is in this last stage that the great certainty of the law has been established, which stamps it as the supreme law of

physical science It is interesting also to notice how the law, which had its roots in engineering practice and was developed primarily for engineers, has become of such fundamental importance and found such widespread application in physical science This is yet another illustration of the principle that in the search into the unknown, no possible avenue, no clue—that is likely to be fruitful, can be neglected We can never be certain in what direction the hidden treasure lies and so it behoves us to search all places diligently.

EXAMPLES ON CHAPTER XIII

1 Give an account of a vapour-compressing refrigerating machine, and show how its action illustrates the principles of thermodynamics (*Camb Schol*)

2 Distinguish between a reversible and an irreversible cycle. Explain carefully the physical conditions essential for reversibility

Illustrate by means of a pressure-volume diagram the cycle of changes in a four-stroke gas explosion engine (*Oxford Schol*)

3 What is meant by a reversible change? Show that the efficiency of a reversible heat engine working between two specified temperatures is a maximum for those temperatures, and deduce an expression for the efficiency in terms of the temperature scale you adopt (*Tripes*, Part 1)

4 What is a cycle process in thermodynamics?

Compare Carnot's cycle with that of any engine with which you are familiar (*Oxford Schol*)

5 Establish *Carnot's principle*, stating clearly the premisses from which you start out (*London B Sc*)

6 Discuss what is meant by Carnot's reversible cycle Show that if Perpetual Motion is impossible, the work done by a reversible engine for a given supply of heat from the boiler will be independent of the nature of the working substance and greater than for any engine which is not reversible

Taking a soap film as the working substance, show that if the surface tension diminishes as the temperature increases a soap film must cool when stretched (*Camb Schol*)

7 Show that all reversible heat engines working between the same two temperatures are of equal efficiency.

Describe Lord Kelvin's absolute scale of temperature (*Camb Schol*)

8 Describe Carnot's engine Point out the conditions which are necessary to make it reversible, and discuss the effects produced when it is reversed

In an ice-house, 10 lb of ice would melt per hour when the outside temperature is 20°C , find the least horse-power which would be required to prevent this loss, the engine working between 20°C and 0°C

$$\begin{aligned} J &= 1400 \text{ ft lb per } 1 \text{ lb degree C,} \\ 1 \text{ H P} &= 33,000 \text{ ft lb per min} \quad (\text{Oxford Schol}) \end{aligned}$$

9 Define a scale of temperature without making use of the peculiarities of any selected thermometric substance

Show (a) that Kelvin's work scale is such a scale, and (b) that the ratio of two temperatures as measured on the Kelvin scale is identical with the ratio of the same two temperatures on the perfect gas scale (*London B Sc*)

10 What is meant by (a) the thermodynamic scale of temperature, (b) the perfect gas scale of temperature, (c) the platinum resistance scale of temperature?

What are the advantages and disadvantages of each? (*Camb Schol*)

11 What is meant by the Second Law of Thermodynamics? Illustrate the way in which it can be applied to obtain quantitative results about some particular problem (*Oxford Schol*)

12 Find an expression for the change in the melting point of a substance with the pressure upon it, stating precisely the units employed in expressing each of the quantities involved Contrast the effects on two classes of substances, illustrating your answer by examples (*London B Sc*)

13 Given that the specific volumes of ice and water at 0°C are 1.0908 and 1.0001 c.c. per gram respectively, prove that the freezing point of water will be lowered by increase of pressure, and calculate the change in freezing point for a change in pressure of 10^6 dynes per sq. cm (*London B Sc*)

14 Show from thermodynamical principles how the relative position on a p, v diagram of isothermals for a substance in the solid and liquid states together depends on whether the melting of the solid is accompanied by expansion or contraction

Indicate on p, v diagrams the shape of isothermals of substances of the two classes (*Tripos, Part 1*)

15 Show that the efficiency of all reversible heat engines working between the same two temperatures is the same, and

deduce a value for the efficiency in terms of the temperature of the source and condenser ,

or,

Discuss the effect of changes of pressure on the boiling-point of a liquid

Assuming that the specific volumes of water and saturated steam at 100°C are 1 cc and 1601 cc respectively, and the latent heat of vaporisation is 536 calories per grm, find the change in the temperature of the boiling point due to a change of pressure of 1 cm of mercury (Camb Schol)

16 What is meant by the "efficiency" of a heat engine? When is an engine said to be reversible? Discuss the conditions of reversibility. With a reversible engine, how would the work got by cooling 1 lb of water from 100°C to 0°C compare with that got by cooling 100 lb of water from 1°C to 0°C ? (Camb Schol)

17 Either write an essay on Entropy ;

or,

Show that the efficiency of a reversible engine working between two temperatures is a maximum, and deduce a value for the efficiency in terms of the temperatures of the source and of the condenser (Camb Schol)

18 The destiny of the physical universe is stagnation. Discuss this statement

19 Give an account of any violations of the second law of thermodynamics which have been suggested, and discuss fully the light which they throw on the real nature of that law

20 State the Second Law of Thermodynamics, and give a critical account of the way in which it arose and the evidence on which it is based.

CHAPTER XIV

CONDUCTION

146. Introductory.—We shall now bring our study of the subject of heat to a close by considering the different ways in which it can be transmitted and the laws which govern them. There are three distinct methods known as **convection**, **conduction**, and **radiation**. The following

definitions are taken from Maxwell's *Heat* since, in the opinion of the author, they form a model of what such definitions should be, and it is safe to say that they have not yet been improved upon

"Convection is the motion of the hot body itself carrying its heat with it" A familiar example of this is the central heating system which is so common in America and is now coming into use in this country A boiler full of cold water is heated by a furnace and the water, on being heated, expands, becomes less dense and rises, its place being taken by colder, denser water from the radiators and the circulating system connected to the boiler In this way a circulation of the water from the boiler to the radiators and back to the boiler again is set up and it is called a "convection current" It will be seen that the water initially in the radiators gets hot, not by staying in the radiator while heat flows to it from the boiler, but by moving on to the boiler to be heated and being replaced by hot water from the boiler The hot body in this case is the hot water in the boiler, and it flows to the radiator "carrying its heat with it" We shall not devote any further space to the consideration of convection, because the simpler examples of it are fully dealt with in elementary text-books, and its more advanced applications refer chiefly to Meteorology, which is now a separate science, and which cannot usefully be dealt with in this book.

The reader may now enquire how the cold water in the boiler of a central heating system itself receives heat That part in close proximity to the furnace gets it by **conduction**, which Maxwell defines as "the flow of heat through an unequally heated body from places of higher to places of lower temperature" When a poker is placed in the fire, the end actually in it becomes hot first and then the other end gradually becomes hot too This is due to conduction of heat along the poker Notice the contrast between this mode of heat transmission and convection There is no question of the end of the poker originally in the fire exchanging places with the handle! The poker as a whole remains fixed, while the heat actually flows through it We see then that conduction can take place in solids as well as in liquids and gases, whereas convection can only occur in liquids and gases.

The third way of transmitting heat is called **radiation**, which Maxwell defines in the following way "In radiation, the hotter body loses heat, and the colder body receives heat by means of a process occurring in some intervening medium which does not itself thereby become hot" This definition is a splendid example of the caution and the power to suspend judgment in the face of insufficient evidence which are essential to the scientific temper Nevertheless, it is in no way ambiguous or confusing It is especially appropriate in view of the modern developments in physics Later definitions than Maxwell's describe radiation as the transmission of heat by its conversion into waves in the ether, which are converted back into heat again on striking any body which can absorb them But there are two objections to such a definition In the first place, a set of facts has recently been discovered which cannot be explained on the view that radiation is waves in the ether and so the nature of radiation is uncertain at the moment Secondly, there are some physicists who still maintain that an adequate picture of the physical world can be formed without postulating the existence of the ether and so it is better to leave out such a term in the definition of radiation It is, in any case, very interesting to observe that Maxwell's definition stands the test of time better than do the more recent attempts. We shall now proceed to the quantitative definition and measurement of conductivity, reserving the treatment of radiation to the next chapter

147. Definition of Thermal Conductivity.—Let us suppose that we have a portion of material of uniform area of cross-section A and length d and that one end of it is maintained at temperature θ_1 and the other at temperature θ_2 This can be done by supplying heat at the hot end and removing it at the cold end at suitable rates. We shall further suppose that arrangements are made to prevent any escape of heat from the surface of the material At first heat will flow from the hot to the cold end and cause a rise in temperature of the intervening parts of the material In fact, if we consider a section enclosed between any two planes P and Q , perpendicular to the length of the material a given distance apart, the heat flowing into

the section at the hotter plane P is greater than that flowing out across the colder plane Q, the excess going to raise the temperature of the section. As the temperature of the section rises, the difference of temperature between the hot end of the material and the plane P decreases, and that between the cold end of the material and the plane Q increases; this causes the heat entering the section PQ in unit time to decrease and that leaving in the same time to increase, until these two quantities become the same. When this stage is reached at all points of the material, there can be no further change in temperature of any part of it and the **steady state**, as it is called, has been reached. The temperature of each part of the material is different, but the temperature of any given part remains constant in time. To use the language of the mathematician, the temperature of a given point is a function of its distance along the length of the material and is independent of time. It is important to notice that, when the steady state is reached, the amount of heat supplied to the material in unit time is the same as that taken from it in the same time and also the same as the amount crossing any plane in it in that time. It is also interesting to observe that the temperatures and the heat flow are independent of the specific heat of the material, since no change in temperature is taking place.

When the above conditions are realised, it is found experimentally that the amount of heat H crossing any plane in the material is proportional to its area of cross-section A and the time t . As a matter of fact the reader should easily be able to see for himself that both of these relations follow from the fundamental axiom of science that the re-establishment of the same conditions produces the same effects. In this case, if 10 calories of heat flow through 1 sq. cm. of the material in 1 sec. under given temperature conditions, 10 calories will also flow through another piece of the same material 1 sq. cm. in area in 1 sec. under the same temperature conditions. If the two pieces are placed side to side, then 20 calories now flow through in 1 sec. and the combination is equivalent to a piece of the material 2 sq. cm. in cross-section, that is, the heat flowing per second is proportional to the area of cross-

section. And the same relation can be established in the case of the time in the same way

We now come to the third relation which is the result of experimental investigation. It states that the heat flowing through unit area of the material in unit time is directly proportional to the temperature difference between its ends and inversely proportional to its length. To sum up, we have, from experimental evidence, that, when the steady state is reached, the heat H flowing across any plane in the material varies directly as A , t , and $\frac{\theta_1 - \theta_2}{d}$, which is called the **temperature gradient** along the material. So we may write .

$$H \propto A \ t \ \frac{\theta_1 - \theta_2}{d},$$

$$\therefore H = K \ A \ t \ \frac{\theta_1 - \theta_2}{d}, \quad . \quad . \quad (84)$$

where K is a constant depending only on the nature of the material and its temperature and is called the **thermal conductivity** of the material.

The name "temperature gradient" is chosen for the quantity $\frac{\theta_1 - \theta_2}{d}$, since it is the rate at which the temperature changes with distance in the direction of the heat flow. In the same way the "gradient" of a hill is equal to the rate at which the height of the hill changes with distance along the level, and the potential gradient of an electric field means the rate at which the electric potential varies from point to point.

There are many cases in which the temperature gradient is not uniform, and it is then necessary to modify the above equation somewhat. We will suppose that the direction of heat flow in the material coincides with the x -axis and that the temperature at the planes x and $x + dx$ is θ and $\theta + d\theta$ respectively. Then the temperature gradient at the plane x is $\frac{d\theta}{dx}$, and the heat flowing past the plane x in time t is given by

$$H = -K \ A \ t \ \frac{d\theta}{dx} \quad . \quad . \quad . \quad (85)$$

The negative sign is inserted since heat is known by experiment to flow from points of high to points of low temperature, or down the temperature gradient, which is in the direction of negative x in this case

Before describing some of the ways of finding the thermal conductivity of different substances, it is as well to insist on the ideally simple heat flow which is implied in this definition of thermal conductivity. It is not the same as that which occurs when a poker is first placed in a fire, and it is not even the same as that attained when the temperature of any point of the poker ceases to change with time, since the poker is losing heat from its surface to the surroundings and hence the heat flowing into any section in unit time is greater than that flowing out in the same time. This is an example of a very common procedure in science, in order to understand a process of everyday occurrence, we are compelled to imagine and investigate a much simpler and therefore rarer process of a similar kind, in order to discover the laws which will enable us to elucidate the commoner and much more complicated phenomenon.

148. The Determination of the Thermal Conductivity of Metals : A Simple Method.—The determination of thermal conductivities naturally divides itself into four classes

(a) Solids which are good conductors, mostly metals and their alloys

(b) Solids which are poor conductors, mostly the non-metals

(c) Liquids

(d) Gases. These are the worst conductors of all, and the determination of their conductivity presents the greatest difficulties

We shall consider in this article a simple method of finding the conductivity of metals, which was designed by Dr G F C Searle of the Cavendish Laboratory, Cambridge, as a class experiment for students. It is a simple method because it aims at realising as far as possible the actual conditions postulated in the definition of thermal conductivity

A cylindrical bar B of the metal under test about 4 cm

in diameter and 30 cm long is suitably mounted and is fitted with a steam chest *S* at one end and a coil *C* of metal tubing at the other end (Fig 97). A steady flow of water can be passed through this coil from a constant head apparatus, and the temperature of the inflowing water is measured by the thermometer T_4 and that of the outflowing water by the thermometer T_3 , each one being so immersed in a tube that the water is compelled to flow round its bulb. The temperature of two points on the bar a known distance d apart is measured by the two

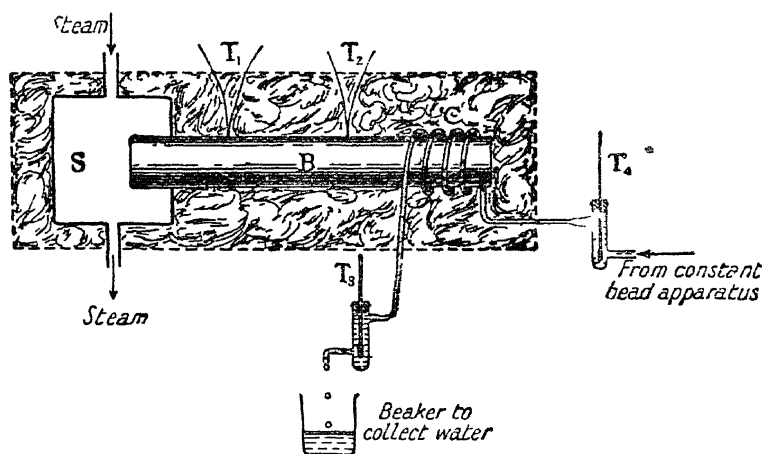


FIG 97

thermometers T_1 and T_2 , which are immersed in mercury cups. They may either be mercury thermometers or thermo-couples, though the latter are preferable since they need much smaller mercury cups and so disturb the flow of heat less. The whole apparatus is "lagged," or heat insulated, to prevent loss of heat from the surface of the bar by enclosing it in cotton wool, whose outlines are represented by the dotted lines. This, in turn, is placed in a wooden box, which is not shown in the diagram.

We commence the experiment by turning on the steam and the steady flow of cold water, and we then wait until the reading of all the thermometers is constant, which

indicates that the steady state has been reached. The readings θ_1 , θ_2 , θ_3 , and θ_4 of the thermometers T_1 , T_2 , T_3 , and T_4 respectively are taken, and the mass M of cold water circulating round the coil C in a time t is found by collecting it in a beaker, which is weighed before and after.

Since we did not take our readings until the steady state was reached and there is no loss of heat from the surface of the bar, we may use equation (84). So we have

$$\frac{H}{t} = KA \frac{\theta_1 - \theta_2}{d}.$$

But in this case $H = M(\theta_3 - \theta_4)$ since the heat withdrawn from the bar in time t is the same as that flowing past any plane in the bar in the same time

$$\therefore \frac{M(\theta_3 - \theta_4)}{t} = KA \frac{\theta_1 - \theta_2}{d},$$

from which K , the thermal conductivity of the metal under test between the temperatures θ_1 and θ_2 , can at once be calculated.

The method can be somewhat improved by substituting an electrically heated coil for the steam chest S , thus enabling the heat supplied to the bar in time t to be calculated as well as that taken from it by the circulation of cold water. These two quantities should be equal if there is no loss of heat from the surface of the bar, and so this point can be tested. If there is any such loss, the mean of the heat supplied and that withdrawn should be taken as that flowing past any plane in the bar in the same time. This is not strictly true, but if, as is usually the case, the error involved is less than the other experimental errors, the approximation is justifiable.

149. Forbes' Method.—The advantage of the method designed by Dr Searle, as we have already pointed out, is that it attempts to realise the conditions postulated in the definition of thermal conductivity. But it is a fact that it is quite impossible to do this in practice, since no perfect heat insulator has yet been discovered, and so some escape of heat from the surface of the bar always occurs. So Forbes tried another method which avoids

this difficulty by allowing the heat to escape freely from the surface of the bar, but this introduces a disadvantage in that it is no longer possible to use the simple equation of conductivity

The principle of the method will be understood from Fig 98. A cylindrical bar of the metal under investigation is mounted with one end in a suitable constant temperature bath, such as molten solder, while the rest of the bar sticks out into the open air. When the steady state is reached, the temperature of various points along the bar is measured and a graph of temperature against distance is drawn. It follows from equation (85) that the heat flowing across the plane P in unit time = $-KA \frac{d\theta}{dx}$,

where K is the conductivity of the material of the bar, A is its area of cross-section, and $\frac{d\theta}{dx}$ is the temperature gradient at the point P, which the reader should be able to see is equal to the slope of the temperature-distance graph at that point. This heat is

all lost by emission from the surface of the bar to the left of the plane P and the far end, and the amount so lost in unit time can be calculated if the perimeter of the bar, the temperature of the various points along it, and the emissivity of its surface are known, Newton's law of cooling being assumed to be true. The **emissivity** of the surface is the amount of heat lost in unit time per unit area when the excess temperature of the surface over that of the surroundings is unity. This emissivity has to be determined in a separate experiment, and then the heat lost by emission is equated to that flowing through the plane P, thus giving an expression from which the thermal conductivity can be calculated.

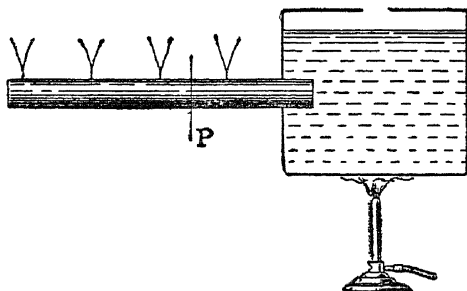


FIG 98

We shall now proceed to the details of the theory of the method, basing it on the general opinion of the flow of heat along a bar. We shall then describe the two experiments which have to be performed to enable the conductivity to be calculated.

Let us suppose that the axis of the bar of metal is taken as the x -axis of a set of co-ordinates, the origin being at the hot end of the bar, which is placed in the direction of negative x , so that the temperature increases as x increases algebraically (Fig 99). Consider two planes perpendicular to the axis of the bar at $-x$ and $-(x+dx)$, at which the excess temperature of the bar over the surroundings is θ and $\theta - d\theta$ respectively. The heat flowing in unit time across the first plane in the direction of

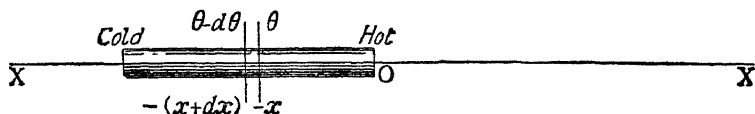


FIG 99

positive $x = -KA \frac{d\theta}{dx}$. The negative sign appears because $\frac{d\theta}{dx}$ is itself positive, but the heat flow is in the direction of negative x . The heat flowing in unit time across the second plane in the direction of positive $x = -KA\{\text{temperature gradient at } -(x+dx)\}$. If we denote temperature gradient by the letter y for the moment, then

$$\text{temperature gradient at the plane } -x = \frac{d\theta}{dx} = y,$$

$$\begin{aligned} \therefore \text{temperature gradient at the plane } -(x+dx) &= y + \frac{dy}{dx} - dx \\ &= y - \frac{dy}{dx} \quad dx = \frac{d\theta}{dx} - \frac{d}{dx} \left(\frac{d\theta}{dx} \right) dx = \frac{d\theta}{dx} - \frac{d^2\theta}{dx^2} dx \end{aligned}$$

Therefore the heat flowing in unit time across the second plane in the direction of positive $x = -KA \left(\frac{d\theta}{dx} - \frac{d^2\theta}{dx^2} dx \right)$

Now the difference between the heat flowing across the plane $- (x + dx)$ in the direction of positive x in unit time and that flowing across the plane $- x$ in the same direction in the same time is equal to the excess of the heat flowing into the portion of the bar included between the two planes over that flowing out in unit time and is given by

$$\begin{aligned} & -KA \left(\frac{d\theta}{dx} - \frac{d^2\theta}{dx^2} dx \right) - \left(-KA \frac{d\theta}{dx} \right) \\ & = +KA \frac{d^2\theta}{dx^2} dx \end{aligned}$$

When the steady state is reached, this excess is lost by emission from the surface of the bar. By Newton's law of cooling, the heat so lost in unit time $= Ep\theta dx$, where p is the perimeter of the bar and E the emissivity of its surface. It will be remembered that θ denotes the *excess* temperature of the bar over its surroundings

$$\begin{aligned} \therefore KA \frac{d^2\theta}{dx^2} dx &= Ep\theta dx, \\ \therefore \frac{d^2\theta}{dx^2} &= \mu^2\theta \quad . \quad . \quad . \quad (86) \end{aligned}$$

where

$$\mu^2 = \frac{Ep}{KA}.$$

To solve this differential equation try

$$\theta = Ae^{mx} \quad . \quad . \quad . \quad (87)$$

where A is an arbitrary constant and m is a constant to be determined in terms of μ , the only constant in the differential equation. Differentiating equation (87) twice with respect to x , we have

$$\frac{d^2\theta}{dx^2} = m^2 Ae^{mx}.$$

Substituting these values of $\frac{d^2\theta}{dx^2}$ and θ in equation (86), we have

$$\begin{aligned} m^2 Ae^{mx} &= \mu^2 Ae^{mx}, \\ \therefore m^2 &= \mu^2, \\ \therefore m &= \pm \mu. \end{aligned}$$

So equation (87) is a solution of the differential equation, provided that we put $m = \pm \mu$. So we see that there are two possible solutions,

$$\begin{aligned}\theta &= Ae^{+\mu x}, \\ \theta &= Be^{-\mu x}.\end{aligned}$$

The reader will appreciate that the solving of a differential equation is really a rather complicated kind of integration. Since each integration introduces one arbitrary constant and a second order differential coefficient is present in equation (86), the solution of the equation is equivalent to two integrations and so must include two arbitrary constants. The most general solution of the equation can therefore be written

$$\theta = Ae^{\mu x} + Be^{-\mu x}, \quad . \quad . \quad . \quad (88)$$

where A and B are arbitrary constants, corresponding to the constants of integration. The reader should verify that this equation is a solution of the differential equation by differentiating twice and substituting.

The arbitrary constants are only fixed when the initial conditions are decided upon. In this case, when $x = -\infty$, $\theta \neq \infty$, and when $x = 0$, $\theta = \theta_0$, say. When $x = -\infty$,

$$\begin{aligned}\theta &= Ae^{-\mu \infty} + Be^{+\mu \infty}, \\ \therefore \theta &= Be^{+\mu \infty}\end{aligned}$$

Since μ is necessarily positive, if $\theta \neq \infty$, then $B = 0$.

From the second condition, we have

$$\theta_0 = A$$

So the solution of the differential equation appropriate to the conditions of Forbes' experiment is

$$\theta = \theta_0 e^{+\mu x} \quad . \quad . \quad . \quad (89)$$

It is convenient to re-write this in the form obtained by taking logarithms, when we have

$$\begin{aligned}\log_e \theta &= +\mu x + \log_e \theta_0 \\ \text{or} \quad \log_e \theta &= +\mu x + \text{a constant} \quad . \quad . \quad . \quad (90)\end{aligned}$$

It should be noticed that equation (89) does not imply large values of θ , since it only applies to negative values of x .

150. Forbes' Method: The Statical Experiment.—

The first experiment which has to be performed in Forbes' method is called the statical experiment, since all the temperatures are stationary when the readings are taken. The apparatus is shown in Fig 98 and consists of a bar of the metal under investigation, several feet long, mounted with one end in a suitable constant temperature bath and the other sticking out into the air. The bar is left until the temperature of every point of it is steady, that is, until the steady state is reached. The temperature of several points equally spaced along the bar is then read by means of thermo-couples. It may be pointed out that it is difficult to realise the steady state in practice, since draughts and other disturbances cause sudden changes in temperature at some point in the bar, which are propagated along the bar as temperature waves and are not damped out for some time. A graph is then drawn of $\log_e \theta$ against x , and it can be seen from equation (90) that it should be a straight line of slope $+\mu$. In this way the value of μ can be obtained from the statical experiment.

But $\mu^2 = \frac{E\rho}{KA}$ and so to find K from it, it is only necessary to know the area of cross-section and perimeter of the bar and the emissivity of its surface. This latter quantity is determined in the **dynamical experiment**, which will now be described.

151. Forbes' Method: The Dynamical Experiment.—This experiment is so called since the temperatures are varying in time when the readings are taken. A portion of the original bar is needed or, if this is not available, a piece of the same metal of precisely the same surface. That is, if the surface of the original bar is polished, that of the other specimen must be polished also. The specimen is raised to a temperature as high as that used in the statical experiment, care being taken to see that all parts of it are at the same temperature. It is then removed from the heater and mounted on two badly conducting knife-edges, and allowed to cool by emission from its surface. Its temperature is read at various intervals of time by means of two or three thermometers placed at various points in the specimen. From these readings a graph of temperature

against time is drawn and tangents are constructed to it at various points so as to obtain the rate of loss of temperature for various excess temperatures. In this way the average rate of loss of temperature for a unit excess temperature can be calculated, assuming Newton's law of cooling to be true. If the mass, specific heat, and total area of surface of the bar are known, the rate of loss of heat per unit area per unit excess temperature, that is the emissivity, can be calculated.

Substituting this value of the emissivity and the area of cross-section and perimeter of the bar used in the statical experiment in the expression for μ , K the conductivity of the bar can be calculated. The result gives the average conductivity between the highest and lowest temperatures of the bar in the statical experiment.

The theory on which the calculation of conductivity is based assumes both that conductivity is independent of temperature and that Newton's law of cooling is true for large excess temperatures. That neither of these things is true is shown by the fact that the graph of $\log_e \theta$ against x in the statical experiment is not a straight line, nor is the rate of loss of heat per unit area in the dynamical experiment proportional to the excess temperature at high temperatures. But the method can be applied without serious error by restricting ourselves to such a small length of the bar that the conductivity and emissivity are sensibly constant over it. In this way the conductivity of the material for various ranges of temperature can be calculated, and it is found to decrease with rise of temperature.

Forbes' method is not very satisfactory since it is impossible to obtain a really steady state in the statical experiment. It is difficult to keep the temperature of the bath of molten solder the same and to realise steady cooling conditions. So his method has been superseded by one due to Professor Lees, which can be used over a wide range of temperature.

152. Lees' Method for Metals.—The methods so far described are only suitable for high temperatures and only determine the average conductivity over a fairly wide range of temperature. So they are unsuitable for the investigation of the variation of conductivity with

temperature We shall now describe a method due to Lees, which can be used over a wide range of temperatures and only needs a temperature difference of a few degrees between the ends of the specimen, it is therefore suitable for an accurate investigation of the variation of conductivity with temperature The apparatus is shown in Fig 100, and consists of a copper frame M, in which a specimen of the material under test can be fitted This is about the size of a lead pencil, that is, 0.5 cm in diameter and 7 cm long It is fitted with a heating coil D and two platinum resistance thermometers E and F to measure the temperature of two points a known distance apart The whole apparatus is mounted inside a Dewar flask so that it can be brought to and maintained at any suitable temperature

We commence the experiment by immersing the apparatus in liquid air until it is somewhat below the desired temperature, when the liquid air is poured out of the Dewar flask and the apparatus is brought to the precise temperature desired by heating it up with an electric current passing through a coil on the outside of the copper frame (This coil is not shown in the diagram) The heating current is then switched on in the coil D, and both it and the P.D. across the coil are measured The current is left running until the difference in temperature between the two thermometers E and F is constant, when the temperature recorded by each is measured Assuming that the steady state has been reached, we have

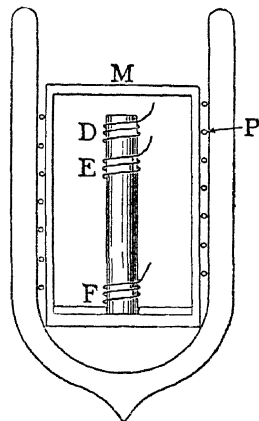


FIG 100.

$$H = KA \frac{\theta_1 - \theta_2}{d} t,$$

where θ_1 and θ_2 are the temperatures of the bar at E and F respectively, a distance d apart,

A is the area of cross-section of the specimen,

H is the heat supplied to it in a time t ,

K is the conductivity of the material between θ_1 and θ_2 ,

But $H = \frac{VCt}{J}$ calories, where V and C are the P.D and current respectively in the coil D, and J is the number of joules in 1 calorie

$$\therefore \frac{VC}{J} = KA \frac{\theta_1 - \theta_2}{d} \quad \cdot \quad \cdot \quad (91)$$

Since all the quantities in this equation are known except K, it can at once be calculated

There is, however, an important correction to be made. The above calculation is only valid if there is no escape of heat from the surface of the specimen and the steady state has been reached. The first condition is ensured by the apparatus being in a Dewar flask, but a moment's thought will show that the second can never be true. For the heat supplied to the specimen by the electric current flowing through the coil D is not removed completely, for it flows into the frame M and raises its temperature. This, in turn, reacts back on to the specimen and raises the temperature of the cold end and ultimately of the whole of it. We see that the temperature of the whole specimen is slowly rising due to what is, in effect, a backward flow of heat from the frame to the specimen. This will obviously cause the difference in temperature between E and F to be less than it would be in the steady state, and we have to find what correction to add to the measured value in order to obtain this "steady state" value. This is done in the following way. A coil P of the same resistance as D is wound round the frame M and the heating current is passed through this, until the temperature difference between E and F is constant, before it is passed through D in the main experiment. As the same current is being passed through a coil of the same resistance, the same amount of heat per unit time is being supplied to the apparatus as reaches it through the specimen in the main experiment. The temperature difference, $d\theta_1$, between F and E, F being now the hotter, is measured. The same process is repeated after the current has been

passed through D and the new temperature difference, $d\theta_2$, between F and E is measured. Then the temperature difference which would exist between E and F in the steady

state is $(\theta_1 - \theta_2) + \left(\frac{d\theta_1 + d\theta_2}{2}\right)$, and this value is used

in equation (91) instead of $(\theta_1 - \theta_2)$. Lees' experiments extended from -170°C to 18°C and to a number of metals and form the basis of a valuable classification of the facts concerning the conductivity of metals.

153. Lees' Disc Method for Non-metals.—The earliest attempts to measure the conductivity of the non-metals showed that it is about fifty times less than that of the metals, and so different methods must be adopted. It is evident that the shape of the specimen will have to be very different, if a bar is used, then it will be impossible to measure accurately the small rate of flow of heat which will be obtained with a reasonable temperature difference between its ends. On the other hand, if we try to increase the rate of flow of heat, we shall be forced up to a temperature difference which may make the hot end inconveniently hot or perhaps even cause the material to melt. Reference to equation (84) shows that if K is small, the rate of flow of heat H can be kept at a reasonable value without too big a temperature difference by decreasing d and increasing A , that is, we must substitute a disc for a bar. This was done by Lees both for non-metals and liquids, and we shall now describe his method for the non-metals.

His apparatus consists of three copper discs, D_1 , D_2 , and D_3 , and a disc M of the substance under investigation, each about 4 cm in diameter and 1 or 2 millimetres thick (Fig 101). The discs are fastened together and a thin coating of glycerine is placed between each disc to ensure good thermal contact. A heating coil is placed in between and insulated from the discs D_1 and D_2 , and the temperature of D_1 and each face of M is measured by thermo-couples

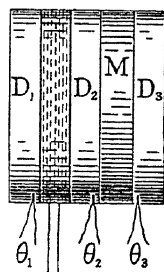


FIG 101.

placed in small holes drilled in the edges of the copper discs. The whole surface of the apparatus is varnished so as to give it the same emissivity and it is then hung in a constant temperature enclosure. The heating current is then switched on and the temperatures θ_1 , θ_2 , and θ_3 are read when the steady state is reached. The current C through the heating coil and the P.D. V across it are read at the same time.

The principle by which we shall calculate the conductivity of the material of M from these observations is that the heat flowing through any plane in the disc M in unit time is equal to the amount of heat emitted from the surface of D_3 in the same time. It will be seen that we require to know the emissivity, e , of the surface, which we can obtain at once from the fact that all the heat supplied electrically in a given time is emitted from the surface of all the discs in the same time. If A_1 , A_2 , and A_3 are the areas of the discs D_1 , D_2 , and D_3 respectively from which heat is emitted, α the corresponding area in the case of M and θ_0 is the temperature of the enclosure, we have, assuming Newton's law of cooling to be true as the temperatures are not high,

$$\frac{VC}{J} = e \left\{ A_1(\theta_1 - \theta_0) + A_2(\theta_2 - \theta_0) + \alpha \left(\frac{\theta_2 + \theta_3}{2} - \theta_0 \right) + A_3(\theta_3 - \theta_0) \right\}$$

from which e can at once be calculated. Using this value of e , we then proceed to calculate the conductivity K from the equation

$$KA \frac{\theta_2 - \theta_3}{d} = e \left\{ \frac{\alpha}{2} \left(\frac{\theta_2 + \theta_3}{2} - \theta_0 \right) + A_3(\theta_3 - \theta_0) \right\}$$

where A is the area of cross-section of M and d is its thickness. It will be seen that we have included half the heat emitted from the surface of M in the expression for the heat emitted. This is because the expression for the heat crossing any plane of M is the average of that entering and leaving M , and some of this is lost by emission from its surface. The reader will naturally wish to know the purpose of the discs D_2 and D_3 . He will be tempted to ask why the heating coil is not applied directly to the surface of M , and why

emission of heat is not allowed to take place directly from its surface. The answer is that we can only use the simple equation of conductivity if the flow of heat is normal to the faces of the disc M , that is, if the temperature all over any plane parallel to its faces is the same. Since the material of M is a bad conductor, it is evident that this condition is going to be very difficult to obtain, since a bad conductor can support considerable differences in temperature without a big flow of heat. The copper discs serve to prevent such differences of temperature from establishing themselves. For, if such a difference is set up between two points of M , the same difference at once occurs between the two points of the copper disc in contact with them. But copper is a good conductor, and so heat at once flows from the hot to the cold point through the copper until the temperature difference has been destroyed. The copper discs also serve to facilitate the measurement of the temperature of the faces of M . It would be impossible to do this by putting thermo-couples in contact with the faces themselves, but a thermo-couple inserted in the copper disc close to the face will give the temperature of the corresponding face, since copper is such a good conductor.

154. Lees' Disc Method for Liquids.—In considering methods of measuring the conductivity of liquids, we are faced at the outset with the problem of eliminating convection, which will transmit far more heat than conduction. This is shown by the familiar experiment of boiling a test-tube of water with a piece of ice loaded so as to keep it at the bottom. The water can be boiled at the top for quite a time before the ice melts; no convection can take place under these conditions since the hot water is produced at the top and so cannot rise any further, or for that fact sink and "carry its heat with it" to the bottom. Hence we see that water is a bad conductor of heat. We can easily see that convection transmits far more heat than conduction by repeating the experiment with the ice floating at the top of the tube and the bunsen applied at the bottom. The ice will all melt long before the water at the bottom boils. This experiment not only demonstrates our difficulty but suggests the way of overcoming it. We have merely to arrange that the top layer of the liquid

shall be hot with each horizontal layer getting cooler as we go downwards, that is, the temperature gradient must be negative in a vertically downwards direction, and no convection can occur. This device has been adopted in all methods for finding the conductivity of liquids and we shall describe Lees' disc method, which is the most accurate.

The principle of the method is to force heat first through a disc of a solid bad conductor of known conductivity and then through a disc of the liquid under test. If both the area and the temperature gradient of each disc are known, the rate of flow of heat can be calculated from the known conductivity of the solid and used to find that of the liquid. The apparatus is shown in Fig. 102 and consists of a set of discs of about the same size as in Lees' disc method for non-metals and fastened together in the same way. They are mounted horizontally this time and the heat

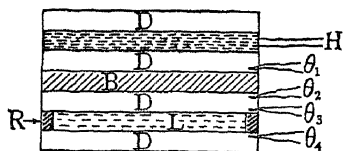


FIG. 102.

flow is downwards through the liquid to eliminate convection. H is the heating coil set between two copper discs. Under the lower one is the disc B of bad conductor, followed by another copper disc D, and the disc of liquid L enclosed in an ebonite ring R, and a

final copper disc. Thermo-couples are inserted as shown to take the temperature of the faces of B and L. The surface of the whole apparatus is varnished and mounted in a constant temperature enclosure.

The procedure in the experiment is to switch on the current in the heating coil and read the four thermometers when the steady state has been reached. Then, if K_1 , A_1 , and d_1 are the conductivity, area of cross-section, and thickness respectively of B and the same letters without subscript and with the subscript 2 denote the corresponding quantities for the liquid and the ebonite ring respectively, the heat flowing across any plane in B per second

$$= K_1 A_1 \frac{\theta_1 - \theta_2}{d_1}.$$

But this is equal to the sum of the heat flowing across any plane in the liquid and the ebonite ring per second, which is given by

$$KA \frac{\theta_3 - \theta_4}{d} + K_2 A_2 \frac{\theta_3 - \theta_4}{d_2},$$

$$\therefore K_1 A_1 \frac{\theta_1 - \theta_2}{d_1} = KA \frac{\theta_3 - \theta_4}{d} + K_2 A_2 \frac{\theta_3 - \theta_4}{d_2},$$

from which K can at once be calculated. This equation assumes that no heat is emitted from the curved surface of the discs B, D, and R, but the small correction for this can be made, if a high degree of accuracy is required.

155. Laby and Hercus' Experiments on Gases.—In considering methods of finding the conductivity of gases, we are faced not only with the problem of convection, but also that of radiation. For rough preliminary experiments show that the conductivity of gases is so low, that the heat transmitted by this means will not be so much greater than that conveyed by radiation, that the latter can be neglected. Furthermore, it is necessary to enclose the gas in some solid vessel, and the heat transmitted by this will certainly be much greater than that which flows across the gas. Many methods have been devised to overcome these difficulties, and we shall describe the most recent and the most successful, that due to Laby and Hercus.

The principle of their method is to establish a uniform temperature gradient in a horizontal disc of gas contained between two plates, the temperature decreasing as we go downwards to eliminate convection. This simple state of affairs, which the reader will appreciate is the same as that postulated in the definition of conductivity, is obtained by supplying heat electrically to the top layer of gas and removing it at the same constant rate from the bottom layer by water cooling. It is also essential to prevent any escape of heat from the curved surface of the disc of gas and this is done most ingeniously by surrounding it with a "guard-ring" of the same gas, whose temperature decreases as we go downwards and is always at the same temperature as the actual disc at the same horizontal plane (Fig 103). This "guard-ring" also ensures that the

lines of heat flow are parallel to the axis of the disc all over its surface, the tendency of the lines to bulge outwards

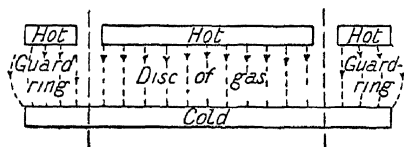


FIG 103.

being transferred to the outside of the guard-ring itself. The apparatus is shown in Fig 104 and consists of a heating coil placed between two copper plates Q, which are planed flat and silvered so as to reduce radiation

to a minimum. The gas under test is contained between Q and another copper plate R, whose surface is also plane and silvered, and which is cooled by a stream of water passing along its lower surface. In order to prevent any of the heat generated in the heating coil from flowing upwards, another plate P is mounted above Q and is kept at the same temperature. In order to prevent any of the heat generated in the coil in Q from flowing down the

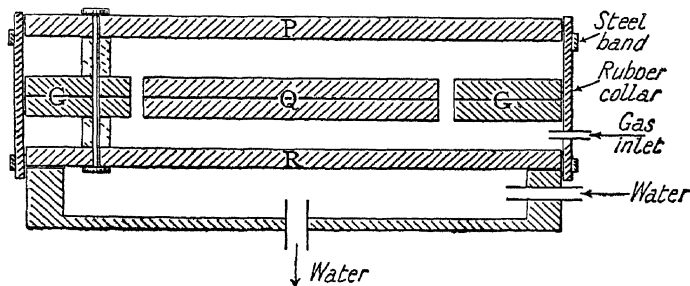


FIG 104.

walls of the containing vessel and also to keep the lines of flow of heat everywhere normal to the face of Q, a metal ring G is placed round the outside of Q and maintained at the same temperature by a separate heating coil. The gas between this ring and the outer parts of R also serves as the "guard-ring" mentioned above to prevent the escape of heat from the surface of the "disc" of gas under test, thus ensuring that the rate of flow of heat across any plane in the gas is the same and therefore that the

temperature gradient is uniform. The plate Q is attached to the guard-ring by three ivory buttons, and the plates P, G, and R are clamped together by three screws separated by glass distance pieces. The apparatus is made gas-tight by enclosing it in a stout rubber collar secured by two steel bands. The distance from Q to R is about 6 mm and a temperature difference of about 20° C was used.

The procedure in the experiment is to switch on the heating currents in Q, G, and P and set the stream of water flowing past R. When the steady state has been reached, the temperature of Q and R is read by thermo-couples attached to them. It is interesting to notice that these thermometers were made of copper and constantan, the copper plates themselves acting as one metal of the thermo-couple. We calculate the conductivity of the gas from the equation

$$\frac{VC}{J} = KA \frac{\theta_1 - \theta_2}{d},$$

where V and C are the P D and current respectively through the heating coil in Q,

A is the mean of the areas of cross-section of Q and the hole of the guard-ring,

θ_1 and θ_2 are the temperatures of Q and R respectively, and d is their distance apart.

A correction must be subtracted from VC for the heat transmitted from Q to R by radiation. It is found to amount to about 5 per cent of the whole, and the details of the way in which it is calculated can be obtained in Roberts' *Heat and Thermodynamics* or in the original paper.

The value of the conductivity of a few typical substances is given in Table XI.

156. Theories of Conduction.—We have already seen in Art 92 in Chapter IX on the kinetic theory of matter how the qualitative fact of conduction can be explained by the transmission of the greater kinetic energy of the molecules at the place of high temperature to that of low temperature by encounters between the molecules and actual transfer of molecules in the case of gases and liquids and by encounters only in the case of solids. In attempting to place this theory on a quantitative basis, we must first

TABLE XI — THE THERMAL CONDUCTIVITY OF VARIOUS SUBSTANCES

Substance	Thermal Conductivity Cals per sec per sq cm per unit temperature gradient
Silver . .	1 01
Copper . .	0 92
Cast iron . .	0 114
Pure lead . .	0 083
Crown glass	$2 5 \times 10^{-3}$
Oak . .	$0 6 \times 10^{-3}$
Ebonite . .	$0 4 \times 10^{-3}$
Cotton . .	$0 55 \times 10^{-3}$
Mercury . .	0 015
Water	$1 31 \times 10^{-4}$
Glycerine . .	$6 8 \times 10^{-4}$
Turpentine	3×10^{-4}
Hydrogen	$31 8 \times 10^{-5}$
Air . .	$5 40 \times 10^{-5}$
Carbon dioxide	$3 07 \times 10^{-5}$

classify the facts we have collected so far. We are assisted in this attempt by noticing that good conductors of heat are also good conductors of electricity and vice versa. This general resemblance between the two phenomena was induced by **Wiedemann and Franz** into quantitative law which bears their name and states that the ratio of the thermal to the electrical conductivity of all metals at a given temperature is proportional to the absolute temperature, the constant of proportionality being the same for all, or mathematically

$$\frac{K}{\sigma} = \alpha T,$$

where K and σ are the thermal and electrical conductivity respectively of a metal at absolute temperature T and α is a constant, which is the same for all metals. This law fits

the facts very well at ordinary temperatures, but definite deviations occur at low temperatures, as is shown by Table XII, which is based on Lees' results of K for metals

TABLE XII —To ILLUSTRATE WIEDEMANN AND FRANZ'S
LAW

$\frac{K}{\sigma T} \times 10^8$ K in watts per centimetre-degree, σ in reciprocal ohms per centimetre cube

Metal	Lees' Direct Method				
	- 170° C	- 100° C	- 50° C	0° C	18° C
Aluminium	1 50	1 81	1 98	2 09	2 13
Copper	1 85	2 17	2 26	2 30	2 32
Silver	2 04	2 29	2 36	2 33	2 33
Zinc	2 20	2 39	2 40	2 45	2 43
Lead	2 55	2 54	2 52	2 53	2 51
Iron	3 10	2 98	2 93	2 97	2 99
Manganin	5 94	4 16	3 58	3 41	3 34

It may be mentioned that Wiedemann and Franz formulated the law before Lees had done his work on metals

We must now see if this law can be explained on the kinetic theory of matter. The conduction of electricity by metals has been explained by assuming the existence in such metals of **free electrons**, that is, electrons which are only loosely bound or not bound at all to any particular atom. In the absence of an electric field these electrons are supposed to possess the velocity of thermal agitation appropriate to their mass and temperature, in fact, they behave like the molecules of an ideal gas. If an electric field is established in the metal in a particular direction, these free electrons will be acted on by a force in that direction and they will commence to drift as a whole along the negative direction of the field. It is this drift of the electrons which constitutes the electric current in a solid conductor. It has been found possible to explain Ohm's law and to explain the order of magnitude of the observed conductivities, if it is assumed that there is about one free electron per atom.

Since the free electrons behave like the molecules of an ideal gas, it is evident that they will assist in the conduction of heat along the metal. For the free electrons at the hot end of a metal bar will have, on the average, a greater kinetic energy of thermal agitation than those at the cold end, and they will pass it on both by encounters and by the transfer of electrons from the hot to the cold end due to their random motion. Assuming that the whole of the conduction of heat in metals is due to the free electrons, an expression for the thermal conductivity can be obtained working on these lines and this, together with the expression for the electrical conductivity, leads to Wiedemann and Franz's law, the value of the constant showing satisfactory agreement with that determined experimentally. We should not expect precise agreement, since some of the heat is conducted by the passing on of the energy of vibration of the atoms, and we have taken no account of this contribution.

A very serious difficulty faces this theory, however. Since the free electrons behave like the molecules of an ideal gas, their energy varies with temperature, and if there are enough of them it must make a contribution to the specific heat of good conductors and cause it to be greater than that of bad conductors. As a matter of experiment no such difference is observed, although the number of free electrons required to explain electrical conductivity should cause a difference of about 3 calories per gram-atom. The way to further progress along these lines seems barred, for the specific heat difficulty can only be removed by assuming that the energy of the free electrons is independent of temperature, which at once makes them unable to help in the conduction of heat¹. This is disappointing in view of the success so far obtained, but an explanation has been obtained on the quantum theory as to why the free electrons make no contribution to the specific heat of the metals. It cannot be said that this explanation is yet accepted as true, but it is probable that a solution of the difficulties will be found along these lines.

No classification of the facts concerning the conductivity of liquids has yet been made, and there exists no quantitative theory of the conduction of heat in liquids. We

may conclude by reminding the reader that it was shown in Art 106 that, on the kinetic theory, the conductivity of gases should be independent of pressure, a prediction which has been accurately and comprehensively verified by experiment. The verification of this prediction is one of the triumphs of the kinetic theory, and with it we conclude this account of the conduction of heat.

EXAMPLES ON CHAPTER XIV

1 Define thermal conductivity

Describe a method of measuring the thermal conductivity of a copper rod (*O and C*)

2 Give an account of a method of comparing the thermal conductivities of two metals in the form of rods

The thickness of the ice on a lake is 5 cm and the temperature of the air is -10°C . At what rate is the thickness of the ice increasing, and approximately how long will it take for the thickness of the ice to be doubled?

(Thermal conductivity of ice = 0.004 cal per sec per cm per $^{\circ}\text{C}$. Density of ice = 0.92 gm per cc. Latent heat of ice = 80 calories per gm.) (*O and C*)

3 Give an account of the theory and experimental details of Forbes' method of measuring the thermal conductivity of a metal rod.

4 Find an expression for the temperature at a point along an infinitely long metal bar which is maintained at a fixed high temperature at one end (*Oxford Schol*)

5 Illustrate by diagrams the variation of temperature along (a) a uniform bar, (b) a compound bar consisting of two bars of different materials and the same cross-section placed end to end

(1) when the bar is jacketed (to prevent surface loss), the two ends are kept at fixed different temperatures and a steady state has been attained,

(2) when the bar is unjacketed and the conditions are as above (*Tripos, Part I*)

6 Describe a method which can be used to investigate the variation of the thermal conductivity of metals with temperature

7 Give a critical comparison of the three ways given in this book of finding the thermal conductivity of metals

8 Define thermal conductivity and explain how the conductivities of (a) good conductors, (b) bad conductors may be measured (*Tripos, Part I*)

9 Give a detailed account of a method of determining the thermal conductivity of a bad conductor (*Tripos, Part 1*)

10 How may the conductivity for heat of bad conductors be measured?

"The best method of obtaining an even temperature in an enclosure is to surround it with alternate layers of good and bad conductors" Discuss this statement (*Camb Schol*)

11. Describe and give the theory of a method useful for a practical determination of the thermal conductivity of a liquid (*London B Sc*)

12 Define thermal conductivity

The inner surface of a long hollow cylinder is maintained at a temperature t_1 , while that of the outer surface is maintained at a temperature t_2 . Find an expression for the heat passing per second from the inside to the outside surface of the cylinder in terms of the thermal conductivity k , the axial length l and the inner and outer radii a and b (*Camb Schol*)

13 Define thermal conductivity

The inside of a hollow copper sphere is maintained at 100°C and the outside at 0°C . If the internal radius of the sphere is 2 cm and the external radius 3 cm, find the amount of heat conducted through the sphere per second when the steady state has been reached (Thermal conductivity of copper = 0.91 C.G.S. units) (*Camb Schol*)

14 Define thermal conductivity

A copper tube has an internal radius of 2 cm and an external radius of 2.5 cm. The inside of the tube is maintained at 100°C and the outside at 20°C . Calculate the quantity of heat conducted through unit length of the tube per second (Thermal conductivity of copper = 0.91 C.G.S. unit) (*Camb Schol*)

15 Define the thermal conductivity of a given material

A copper boiler, the area of whose bottom is 12 square feet, boils away 400 lb of steam at atmospheric pressure every hour. The thickness of the bottom of the boiler being $\frac{1}{2}$ inch, find the temperature of the bottom of the boiler on the furnace side (The Latent Heat of steam is 540 in Centigrade units. The thermal conductivity of copper is 0.0072 in inch-second-units) (*Camb Schol*)

16 Define conductivity for heat and describe briefly how

it may be measured experimentally either for a good conductor or for a bad conductor. If the air temperature remains constant at -10°C find the increase in thickness of the ice on a pond between 7 p.m. and 7 a.m. if the initial thickness was 10 cm (Conductivity of ice = 0.005 cal per

sq cm per unit Centigrade temp gradient Density of ice = 0.917 gm per cc Latent heat of ice = 80 calories per gm) (*Camb Schol*)

17 A cylindrical tube of length l , internal radius a , external radius b , and thermal conductivity, k , has its inner surface kept at $t_1^\circ \text{C}$, and its outer surface at a lower temperature $t_2^\circ \text{C}$. How much heat is conducted through the walls of the tube per second?

Show how this principle could be used to determine the thermal conductivity of a bad conductor. Why is the method unsuitable for a good conductor? (*Camb Schol*)

18 An electric iron is made up of a heating grid of area 120 sq cm pressed down tightly on a flat base of the same area from which it is insulated by a thin sheet of mica. The thickness of the base of the iron is 0.25 cm, the conductivity of iron is 0.14 cgs units, the power dissipated in the heating element 350 watts. The temperature drop across the mica is negligible and all the heat may be supposed conducted through the base. Calculate (a) the temperature of the element if the lower face of the iron is maintained at 150°C , (b) the current which must pass through the grid when put on a 200 volt circuit (1 calorie = 4.2 joules) (*Camb Schol*)

19 A cylindrical bar of iron of length 10 cm and radius 1 cm has a small heating coil of resistance 10 ohms wound round one end. The bar is jacketed so as to prevent loss of heat from the sides or from the heated end. The far end is exposed to the air and is found to acquire a temperature of 30°C when a current of 0.5 amp is passed through the coil, the temperature of the air being 20°C . What is the temperature of the heated end of the bar? If Newton's law of cooling is obeyed at the free end of the bar, what is the temperature at the heated end when the current in the coil is 1 amp?

Conductivity of iron = 0.1 cgs units (gram-calorie)

Mechanical equivalent of heat = 4.2×10^7 ergs per cal
(*Camb Schol*)

20 A stream of water is passed through a glass tube of internal diameter r cm and external diameter s cm at the rate of y cc per second. The outside of the tube is maintained at 100°C , and the water enters at 0°C . Find the rise in temperature of the water as it passes through the tube, the thermal conductivity of the glass being K . (*Oxford Schol*)

21 What do you understand by the coefficient of thermal conductivity?

One end of a cylindrical metal rod, 2 mm in diameter, is screwed into a copper block weighing 132 gm. The other end projects into a steam jacket and can be maintained at

a temperature of 100°C The length of the exposed rod between the steam jacket and the face of the block is 10 cm

When the temperature of the apparatus is 10°C , steam is turned into the jacket and the initial rate of rise of temperature of the copper block is observed to be 1°C per min

Assuming that no heat escapes from the surface of the rod, find

(a) the number of calories of heat passing through the rod from the steam jacket in 1 sec,

(b) the coefficient of thermal conductivity of the material of which the rod is made

(The specific heat of copper is 0.09 cal per gram per $^{\circ}\text{C}$)
(N U J B)

22 Define thermal conductivity

Heat is supplied to a slab of compressed cork, 5 cm thick and of effective area 2 sq metres, by a heating coil spread over its surface. When the current in this coil is 1.18 amp. and the potential difference across its ends 20 volts the steady temperatures of the faces of the slab are 12.5°C and 0°C . Assuming that the whole of the heat developed in the coil is conducted through the slab, calculate the thermal conductivity of the cork

Draw a diagram showing how you would propose to carry out the experiment suggested in this example (N U J B)

23 Give an account of Lees' disc method of measuring the thermal conductivity of a liquid

A piece of ice weighing 1 gram is kept at the bottom of a test-tube 2 cm in diameter, filled with water up to a height of 8 cm. If the top of the water is maintained at 100°C , how long will it take the ice to melt, assuming that there is no thermal communication between the ice and water and their surroundings? (Conductivity of water = 0.0011 cgs units; latent heat of fusion of ice = 80 cal per gram)

24 One surface of a flat metal plate, 1 sq metre in area and 1 cm thick, is maintained at 60°C , while the other is exposed in a room where the temperature is 15°C . The emissivity of the exposed surface of the plate is 0.0006 cal per sq cm per sec per deg $^{\circ}\text{C}$ of excess temperature, while the conductivity of the metal is 0.12 cal per cm per sec per deg $^{\circ}\text{C}$. Find the quantity of heat given to the room per hour

What conclusions can you draw from your calculations concerning the effect on the quantity of heat given to the room of (a) the nature of the surface of the plate, (b) the material of which the plate is made? (N U J B)

25 Describe a method suitable for finding the thermal conductivity of a liquid.

Discuss the difficulties which beset the investigation of the thermal conductivity of gases, and indicate how and to what extent they have been overcome (*London B Sc*)

26 Give a critical account of Laby and Hercus' method of finding the thermal conductivity of gases. Discuss any point of interest which has been found about the thermal conductivity of gases

27 A thermos flask, in which the vacuum has been destroyed, is full of water at 100°C . Find the rate at which heat escapes from the water by conduction through the surrounding air. The length of the flask is 20 cm, and the diameters of the inner and outer vessels are 7.0 and 8.0 cm respectively, the temperature of the outer one being 15°C . You may neglect the heat escaping from the rounded end of the vessel and also through the cork

28 The following results were obtained in a simple laboratory method of finding the thermal conductivity of indiarubber. Steam at 100°C is passed through a rubber tube, 14.6 cm length of which are immersed in a copper calorimeter weighing 234 grm containing 440 grm of water. Readings of the temperature of the water are taken every minute while the steam is being passed through the tubing, and a graph of temperature against time is drawn, from which it is deduced that the temperature of the water and calorimeter rises 0.019°C every second when they are at the room temperature, 22°C . The external and internal diameters of the tube are 1.00 cm and 0.75 cm respectively. Calculate the thermal conductivity of indiarubber. (This makes a very suitable laboratory experiment for the determination of the conductivity of a bad conductor)

29 Discuss any classification of the facts of the conduction of heat and any theories which have been advanced to account for them.

CHAPTER XV

RADIATION

157. Introductory.—We have seen that heat is a form of energy, and we shall conclude with a consideration of another form of energy, called **radiation**, which can be converted into heat and produced from it

The commonest source of radiation is the sun. If a thermometer is placed in the sun's rays, its temperature immediately rises, showing that it is receiving heat from the sun. It is also evident that the energy was not in the form of heat as it travelled from the sun to the thermometer, since it came through empty space most of the way. This energy, which originally existed as part of the sun's vast store of heat, must have been changed into some form which can travel through empty space and be converted back into heat when it strikes any body, such as the thermometer, which can absorb it. This form of energy is called radiation, and we shall study its properties with particular reference to their energy aspect. It is evident from what we have already said that light is one kind of radiation, but we shall see that there are also other forms.

158. The Properties of Radiation—The experimental evidence on which the simple properties of radiation are based can be found in the elementary text-books on heat, and we shall accordingly confine ourselves to stating these properties and giving a brief account of the more important ones.

(a) Radiation travels through empty space with the speed of light.

(b) Radiation is converted into heat when it falls on any body which can absorb it.

(c) Radiation travels in straight lines.

(d) It is reflected according to the same laws as light.

(e) It is refracted according to the same laws as light.

We shall now digress to consider this phenomenon of refraction in rather more detail, as it illustrates an important aspect of radiation. It is well known that if a ray of sunlight is passed through a prism and sent on to a screen, the white light is not only deviated but also split up into the colours of the rainbow, and a spectrum, as it is called, is produced on the screen. If a quartz prism is used for this purpose, it can be shown that the spectrum is not confined to the visible region at all, but continues on each side. For a thermometer with a blackened bulb continues to show a heating effect when it is moved out of the spectrum beyond the red end, showing that the sun is emitting a disturbance, which has all the above properties and so is

radiation, but is different from light. Also if suitable substances are placed beyond the violet end of the spectrum they fluoresce strongly, showing the presence there of another variety of radiation. These two varieties are called **infra-red** and **ultra-violet** radiation respectively from their position with relation to the spectrum. Superficially they would appear to be very different from light, but this experiment shows that the difference between infra-red radiation and light is the same as that between red and violet light. Red light is bent less than violet light by the prism and in the same way infra-red radiation is deviated less than white light. A similar consideration applies to ultra-violet light and visible light.

More recent work has resulted in the discovery of other forms of radiation, of which we may mention **Hertzian waves**, which are used in broadcasting, and **X-rays**, which are of great use in medicine and commerce.

We shall now consider two further properties of radiation, which throw considerable light on its nature. The first of these properties is called **interference** and is best illustrated by the case of ripples on the surface of water. If a needle attached to the prong of a tuning-fork is made to dip into some water and the fork is set vibrating, circular ripples are produced and travel out in all directions over the surface of the water. If a second needle is attached to the prong of the fork, which is again set vibrating, it will be noticed that the surface of the water is covered with moving waves which are crossed by some patches of calm. These patches, which are called **interference fringes**, are stationary and no disturbance takes place over them. They are caused by a crest from one needle arriving simultaneously with a trough from the other, or vice versa, and annulling each other. Hence the water in that place always remains calm. We may sum up this phenomenon by saying that disturbance added to disturbance produces calm, and we can see that such a result suggests a wave motion. Without going into details we may say that precisely the same thing has been produced in the case of light, in the sense that light added to light produces darkness. For, if two narrow slits parallel to and very close to one another are illuminated by the

light from a single slit, which is in turn illuminated by a sodium flame, a screen placed on the other side of the two slits is not uniformly illuminated but is crossed by a set of dark bands, parallel and equidistant, called interference fringes. The fringes at once disappear if one of the two parallel slits is covered up. So it is only light added to light which produces darkness, one source of light alone will not produce the effect. A common example of interference in light is the brilliant colours seen on the surface of a puddle of water. This is due to the fact that there is a very thin film of oil on the surface of the water, and interference occurs between the light reflected from the top and bottom surfaces of the film of oil. Certain colours are removed from the reflected light in this way and so it appears coloured. Fading in the reception of broadcasting is due to the same thing. In most cases the waves from the transmitting station reach the receiving set by two paths, one set coming directly along the ground and the other going up into the sky and being reflected down to the receiving apparatus by a kind of mirror in the atmosphere, called the Heaviside layer. If the receiver happens to be in such a place that a crest of the direct wave reaches it at the same time as a trough from the reflected wave, then these will cancel each other out and little or nothing will be heard. Fortunately the height of the Heaviside layer is continually changing and causing the patches of silence to move also, so the receiver is not likely to remain in one for a very long time, fading is nevertheless a nuisance in wireless reception.

The phenomenon of interference suggests that radiation is some form of waves, and we shall now consider another fact, called **diffraction**, which points in the same direction. It is well known that, if ripples on water pass through an aperture which is large compared to the wave-length of the ripples, they go straight on and a sharp shadow of the edges of the aperture is produced. But if the size of the aperture is reduced until it is of the same order as the wave-length of the ripples, then they travel out in all directions after passing through the aperture and bend round the corners of the obstacles which form it. Precisely the same thing happens in the case of an obstacle.

This bending round the corners of apertures and obstacles is called diffraction, and the rectilinear propagation of light was for a long time a stumbling-block to the acceptance of the view that light is a wave motion. But diffraction has now been established in the case of light, the most striking case being the fact that there is a bright spot of light in the middle of the shadow of a small circular object cast by a point source of light. Another example of diffraction, which serves to measure the wave-length of the various kinds of radiation, is the diffraction grating. The earliest gratings consisted of a number of very fine wires stretched close together on a frame so as to form a set of narrow, parallel, and equidistant slits. The modern form of grating is the same in principle, although it contains as many as 14,000 lines to the centimetre. If a beam of light is sent normally on to such a grating, most of it goes straight through, but a certain amount of diffraction occurs at each slit and causes some of the light to be deviated to either side of the direct beam. It also results in a series of spectra being produced on each side of the direct beam, and the wave-length of the various colours can be calculated from their deviation and the number of lines per centimetre of the grating. In this way the wave-length of the various kinds of radiation mentioned above has been measured, and it has been shown that infra-red radiation has a wave-length of the order of 10^{-4} cms, red light one of 8×10^{-5} cm, violet light one of 4×10^{-5} cm, and X-rays one of the order of 10^{-8} cm.

This very brief summary of the properties of radiation shows that it is a wave motion, and further experiments show that the condition which is being propagated is electric and magnetic fields. At one time it was thought that some medium must be postulated in which the waves are propagated, and so the whole universe was filled with the ether for this purpose. But it has so far proved impossible to find out anything about the ether, and the view is now being put forward that there is no such thing. But the matter is not yet decided and we must be content to leave it at that.

159. Varieties of Radiation.—We have seen that the only *physical* difference between the different kinds of

radiation is a difference in wave-length, but this may result in striking differences in ordinary properties and in mode of production. For example, it is only the narrow region of wave-lengths lying between 4×10^{-5} and 8×10^{-5} cm which has the property of producing the sensation of sight; it is only those wave-lengths shorter than about 10^{-8} cm.

TABLE XIII — VARIETIES OF RADIATION

Name	Range of Wave-Length	Mode of Production.	Simple Properties or Uses
Hertzian waves	0.1 mm to 15,000 metres	Radiated from a circuit in which there is a high frequency alternating current	Used for broadcasting
Infra-red radiation	8×10^{-5} cm up to 0.4 mm	Emitted by hot bodies	No outstanding properties other than those common to all radiation
Light or visible radiation	4×10^{-5} cm to 8×10^{-5} cm	Emitted by hot bodies or by the discharge of electricity in gases at low pressure	Produces the sensation of sight.
Ultra-violet radiation	4×10^{-5} cm to 1.36×10^{-6} cm.	Emitted by certain hot vapours, notably mercury vapour.	Has a marked effect on the ordinary photographic plate, used in medicine for the cure of certain skin diseases and for the improvement of general health
X-rays	10^{-9} cm to 10^{-5} cm	Emitted when electrons strike a metal target.	Penetrates considerable thickness of matter, absorbed by matter in proportion to its density, hence the use in surgery and medicine

which have the property of penetrating large thicknesses of matter. For the sake of completeness we append a table giving the wave-length, mode of production, and properties of the principal varieties of radiation. It should be clearly understood that the division is arbitrary and merely for convenience, there is no natural gap in the range of radiations which is complete and continuous from X-rays to the longest waves used in broadcasting.

160. The Transference of Heat by Radiation.—In the previous chapter we have considered the transmission of heat by conduction, and it is right that we should mention that this is often accomplished by radiation. We have mentioned the case of the sun already, but we may give two other examples. In Laby and Hercus' experiments on the conductivity of gases (Art 155) an estimate had to be made of the amount of heat transmitted from the hot to the cold plate by radiation. This is done by exhausting the space between the two plates and finding the rate at which heat is transferred from one to the other. Radiation is the only possible mechanism in this case, and it is interesting to note that the transmission is done entirely by infra-red radiation, as the temperature of the plates is too low for them to emit any visible radiation.

Another common case of the transmission of heat by radiation is the domestic coalfire. It cannot be convection, since the smoke indicates the direction of the convection current, which is, or should be, up the chimney. It is not conduction, since a fire-screen of glass immediately cuts off most of the heat. If the mechanism were conduction, the substitution of a layer of glass, a fairly good conductor, for a layer of very badly conducting air would result in an increase in the heat transmitted. So the mechanism must be radiation and it is interesting to notice that most of the heat is transmitted by the infra-red waves, as the light gets through the glass screen.

This fact illustrates a point which is of some importance in experiments on radiation. We see that glass is transparent to light while opaque to infra-red radiation. Any lenses or prisms used in experiments on the infra-red must be made of quartz, rock-salt, fluorspar, or sylvine, all of which are transparent both to the visible and the infra-

red On the other hand, a solution of iodine in carbon disulphide is opaque to light while transparent to the infra-red Great progress has been made in recent years in the manufacture of special kinds of glass which are transparent only to a particular region of the spectrum This has opened up the possibility of secret signalling with infra-red waves This requires a powerful source of infra-red radiation, which can only be obtained from a source which is so hot that it also emits light But the light, which would spoil the secrecy, is cut out by the screen of special glass transparent only to the infra-red A corresponding improvement has also been made in the development of photographic plates sensitive to the radiation of particular regions of the spectrum The original plate was sensitive only to the ultra-violet and to a smaller extent to the visible, but plates can now be procured which will give good photographs of the infra-red region of spectra These developments have made it possible to obtain the long distance photographs taken with infra-red radiation which have begun to appear in *The Times* and other papers recently

161. Prévost's Theory of Exchanges.—We shall now turn to the problem which will engage our attention for the rest of this chapter, namely, **how the quantity and quality of the radiation emitted per unit area per unit time by a body depend on the nature of its surface and its temperature.** We mean by the quantity of the radiation the total number of ergs emitted as radiation We mean by the quality how the quantity is distributed among the different wave-lengths, we shall give a quantitative definition of this later (Art 163) Before we can tackle this problem, we must enquire more closely into the process of the transfer of heat by radiation

If a hot body is placed in a room, it immediately cools down to the temperature of the surroundings, after which its temperature remains constant Part of the loss of heat is due to convection and conduction, but some is due to radiation When the body reaches the temperature of the surroundings does this radiation cease, as the convection and conduction do? If we bear in mind that the same result would be obtained if the hot body were separated

from its surroundings by a vacuum, we shall see that it is contrary to the established scientific attitude to suppose that it does. For what causes the hot body to start radiating when it is placed in the enclosure? How can the surroundings have any influence on it when they are separated from it by a finite amount of empty space? What causes it to stop radiating when it has reached the temperature of the surroundings? The temperature of the surroundings has got to influence the body at a finite distance away in empty space if we take the view that radiation only occurs between two bodies at different temperatures. This involves the acceptance of action at a distance which is repugnant to a scientific man, as it implies that either there is no mechanism or it cannot be known. So we suppose that all bodies whose molecules are in motion, that is, which are above the absolute zero, are continually radiating. In the case we are considering, the hot body radiates more energy than it absorbs from that received by it from the surroundings. On the whole it loses heat and so cools down. This continues until it reaches the same temperature as the surroundings, when it radiates as much energy as it absorbs from that received by it from the surroundings. Consequently there is now no net loss or gain of heat and so the temperature of the body remains constant. We see that the equilibrium is **dynamic**, as is the case with a saturated vapour (Art. 94). This view of radiation was first put forward by Prévost and is known as Prévost's theory of exchanges. It may be summed up by saying that it asserts that we only observe the net result of the exchange of radiation between the body and its surroundings. This view of radiation is adopted, firstly, because it fits the facts, and secondly, because it is more in accordance with the scientific attitude than the alternative view, that radiation only occurs when there is a temperature difference between two bodies.

162. Absorption and Emission of Radiation.—Merely common experience tells us that both the quantity and quality of the radiation emitted by a body change with its temperature. For example, as a poker is heated up, it not only gives off more radiation, as we can tell by holding it near to our hand, but it starts at a certain temperature

to emit red light, which was absent at a lower temperature. But, postponing the consideration of the effect of temperature until later, how does the emission of radiation at a given temperature depend on the nature of the body? To make the question quite definite, how does the amount of radiation measured in ergs emitted per sq cm per second at a given temperature depend on the nature of the emitter? In the first place it depends only on the nature of the surface of the emitter. The effect of different surfaces was investigated by Leslie, using a Leslie cube as the source and a thermopile to measure the radiation (Fig 105). The Leslie cube consists of a hollow metal cube, whose four vertical faces are coated with different substances, one being lampblacked, one polished, one painted white,

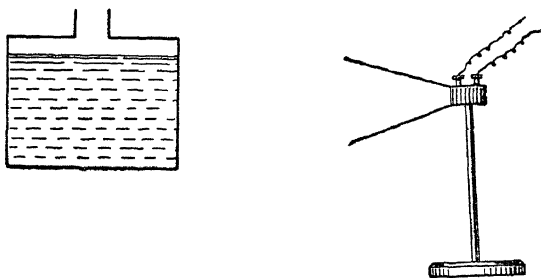


FIG 105

and the fourth left untreated. The thermopile is a set of thermo-couples in series mounted so that the hot junctions all face one way and can be exposed to the radiation, while the cold junctions face the other and are enclosed to keep them at a constant temperature. Radiation falling on the thermopile raises its temperature until it loses heat to the surroundings as fast as it is receiving it from the source of radiation. The difference of temperature so produced is proportional to the amount of radiation received per second, and this temperature difference is proportional to the current produced in the galvanometer. So we may take the deflection of the galvanometer as a measure of the amount of radiation falling on the thermopile per second. The cube is filled with

boiling water and stood such a distance from the thermopile that the largest measurable deflection is obtained with the lampblack surface facing the thermopile. This deflection is noted, and the polished surface is now turned to face the thermopile and the deflection obtained in this case is noted. The same process is repeated for the remaining two faces, the deflections being a measure of the relative amounts of radiation emitted per sq cm per second from the various surfaces when at the temperature of boiling water. It is found that if we arrange the surfaces in order of descending emissive power the following order is obtained: lampblack, untreated surface, painted white, and polished.

The absorptive power of a given surface may be defined as the fraction of the radiation incident on the surface which it absorbs. This quantity can be compared for different surfaces by the following method. Coat the bulb of a thermometer with one of the surfaces to be tested, say lampblack, heat it up to the highest temperature at which it is to be used and place it in the open air, take its temperature at suitable intervals of time and draw up a cooling curve. Now mount the thermometer at a suitable distance from a given source of radiation, which is focussed on to the bulb by a lens. The blackened bulb will absorb a certain fraction of the radiation which falls on it and this will raise its temperature until it is so hot that it loses as much heat by cooling as it is absorbing from the incident stream of radiation. The steady temperature so attained is read, and from the cooling curve, θ_1 , the loss of temperature per second at this temperature can be read off. If W is the water equivalent of the bulb, then $W\theta_1$ is the amount of radiation absorbed by the bulb per second. This whole experiment is repeated in the case of all the surfaces to be tested, a fresh cooling curve being taken for each surface, since the rate of loss of temperature at a given temperature varies for each surface. Then, if θ_2 is the rate of loss of temperature at the steady temperature reached by the thermometer when its bulb is silvered and exposed to the same source of radiation under the same conditions as before, the radiation absorbed per second is $W\theta_2$. Since the amount of radiation falling on the bulb in

each case is the same, the ratio of the absorbing powers of lampblack and silver is

$$\frac{W\theta_1}{W\theta_2} = \frac{\theta_1}{\theta_2}$$

The result obtained is striking, namely, that those substances which are good emitters are also good absorbers, while bad emitters are bad absorbers. If the surfaces are arranged in order of descending emissive power that is also the order of descending absorbing power.

The reader should not be confused by this result which may appear, at first sight, contradictory. He will see that this is not the case if he remembers that the words

absorption and emission do not refer to the net observed gain in heat and the net observed loss in heat but to the total absorption, quite apart from what the surface may be emitting at the same time, and to the total emission, quite apart from what the surface may be absorbing simultaneously. One consequence of this law is that all bodies come to the same temperature if exposed to the same radiation stream, provided that they can only gain

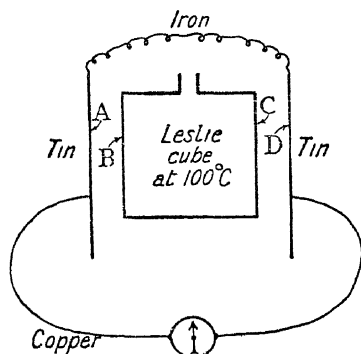


FIG. 106

and lose heat by radiation. For, if the surface of one body absorbs r times as well as that of another, it will obtain r times as much heat in a given time as the other. But it will only reach the same temperature, for it will then be emitting r times as much heat as the other and so will be in equilibrium. This condition is not usually realised in experiments on radiation, as they are not performed in a vacuum, and so most of the loss of heat is due to convection and conduction in the surrounding air.

This conclusion has been verified by Ritchie in another way, and a recent modification of his experiment is illustrated in Fig. 106. Two tin plates are taken, A being

lampblack and D polished. A copper wire is soldered on to each plate so as to form a thermo-couple and the ends are joined to a galvanometer, the circuit being completed by an iron wire. So long as the two plates remain at the same temperature, no current will flow in the thermo-electric circuit and so the galvanometer will register no deflection. We start with the two plates at the same temperature and insert symmetrically between them a Leslie cube filled with boiling water, the polished face B being towards the lampblack plate A and the lampblack face C towards the polished plate D. When this is done, no deflection is produced in the galvanometer, showing that A and D are still at the same temperature. Let us suppose that C emits r times as much radiation per second as B. Then D receives r times as much radiation as A per second. But since the temperature of D remains the same as that of A, it must absorb the same amount of radiation as A per second. Since r times as much radiation falls on it per second, its absorbing power must be r times less than that of A. Hence the zero deflection of the galvanometer indicates that if lampblack emits r times as well as a polished surface, it also absorbs r times as well. That is, a good absorber is a good emitter. In view of the nature of the apparatus used, too much reliance cannot be placed on the quantitative aspect of the result.

A number of interesting examples of this result can be given. Iron is evidently a better absorber than glass for visible radiation, and it is observed that an iron wire glows much more brightly than a thin piece of glass when placed in the same flame. If a piece of porcelain with a pattern which resists heat is raised to incandescence, it will be found that the pattern is reversed, those parts which look darkest when it is cold glowing the most brightly when it is hot. It will be shown below that this relation is true not only of radiation as a whole but of each individual wave-length. Now red glass looks red because it absorbs blue light strongly, consequently it should look blue when it is heated up. The author has never actually seen this effect, as any coloured glass he has been able to obtain has always had its colouring matter destroyed at high temperature.

It should be noticed that our experiments show that the ratio of the absorbing power of two surfaces at a given temperature is the same as that of their emissive powers at the same temperature. But, in all the above examples, the emission occurs at a higher temperature than the absorption. The fact that the results are in accordance with our anticipations shows that the absorbing power of surfaces does not alter radically with temperature. We shall now show that the above facts of emission and absorption can be explained on Prévost's theory of exchanges.

163. The Radiation in a Uniform Temperature Enclosure.—We have seen above that the amount of radiation emitted per sq. cm. per second by a given body depends not only on its temperature but also on the nature of the surface. We now wish to confine ourselves solely to the problem of how the quantity and quality of radiation depend on the temperature, and so it is desirable to find a very general kind of radiation, not one peculiar to a particular type of surface. With this end in view we shall proceed to the consideration of the radiation in an enclosure impervious to heat, whose walls are maintained at a constant temperature. **We shall show first of all that both the quantity and quality of the radiation in such an enclosure depend only on its temperature and are entirely independent both of the nature of the walls and of any substances which may be inside it.**

Let us suppose that we have two such uniform temperature enclosures A and B joined by a tube, which is normally closed by a plate impervious to all radiation, and that the number of ergs of radiation in 1 c.c. of A is greater than that in B although they are both at the same temperature. This quantity is called the **energy density** of the radiation in the enclosure. If we suppose that the window is replaced for a certain time by one transparent to all radiation, it is evident that since more radiation falls on it from A than from B, there will be on the whole a passage of radiation from A to B. Now replace the window impervious to all radiation again and allow A and B to settle into equilibrium with their radiation streams once more. The energy density in A is less than that corresponding to its temperature, and so the walls will on the

whole give radiation to the space in the enclosure and so will cool down. The precise opposite will happen in the case of B. The difference of temperature between B and A which we have produced can be made to supply mechanical work, which has been derived from a source of heat originally all at one temperature. Alternatively we have created a temperature difference between the two enclosures A and B without the expenditure of energy. Either way of looking at the matter shows that it is contrary to the second law of thermodynamics, and so our original assumption that the energy density of radiation in A was different from that in B is incorrect. In fact, the energy density of the radiation in a uniform temperature enclosure depends only on its temperature and is entirely independent of the nature of the walls or of the presence of other bodies in the enclosure.

What we have proved for radiation as a whole can also be established for each infinitesimal band of wave-lengths into which the radiation can be divided merely by substituting for the window transparent to all wave-lengths one transparent only to the band of wave-lengths in question. Hence the energy density of radiation and that associated with each wave-length of the radiation in a uniform temperature enclosure depends only on its temperature, that is, both the quantity and quality of this radiation depend only on the temperature of the enclosure. Such radiation is unique, and we should expect its dependence on temperature to be the simplest of all possible radiations.

164. Kirchhoff's Law.—We shall now use the above result to establish a relation between the emissive and absorptive powers of a substance. Let $e_\lambda \cdot d\lambda$ be the amount of radiation measured in ergs lying between wave-lengths λ and $\lambda + d\lambda$ emitted per sq cm per second by a given body A at temperature T. It is called the **emissive power** of A for the wave-length λ at temperature T. The **absorptive power** a_λ of the body at temperature T for radiation lying between wave-lengths λ and $\lambda + d\lambda$ is defined as the fraction of such radiation falling on the body which it absorbs at that temperature. Let the body be placed in a uniform temperature enclosure at temperature T. We have just shown that its presence does not affect

the radiation stream in the enclosure, and so it must restore to it by emission whatever it takes from it by absorption, when it is in equilibrium. If dQ is the amount of radiation lying between wave-lengths λ and $\lambda + d\lambda$ falling on 1 sq cm of A per second, then it absorbs $a_\lambda dQ$ ergs of this radiation per sq cm per second. It emits $e_\lambda d\lambda$ ergs per sq cm per second. These two must be equal.

$$\begin{aligned}\therefore e_\lambda d\lambda &= a_\lambda dQ, \\ \therefore \frac{e_\lambda}{a_\lambda} &= \frac{dQ}{d\lambda},\end{aligned}$$

which is the same for all substances. Hence

$$\frac{e_\lambda}{a_\lambda} = \text{constant}.$$

This is called **Kirchhoff's law**. Its interpretation is simply that good emitters are good absorbers, which is what Ritchie's experiment showed. Only Kirchhoff's law asserts that the relationship is quantitatively exact, which is more than the experiment could demonstrate with certainty.

We have mentioned a number of interesting examples of Kirchhoff's law before, but we may add one classic example here. When sodium vapour is made to emit light, its visible spectrum consists only of two lines close together in the yellow, that is, it is a good emitter for just these two wave-lengths. By Kirchhoff's law these are the only two wave-lengths which it should absorb. If the light from an arc lamp is passed through relatively cool sodium vapour and analysed in a spectrometer, the continuous spectrum is found to be crossed by two dark lines in precisely the same position as the yellow lines in the emission spectrum of sodium. All the "sodium" yellow light emitted by the arc lamp is absorbed by the cool sodium vapour, whose condition is thereby changed until it emits as much as it is absorbing. But the light emitted by the sodium vapour spreads out equally in all directions and so only a small fraction finds its way to the slit of the spectrometer, which therefore receives much less of the sodium yellow light than it would in the absence of the vapour. So the yellow lines look dark by comparison.

with the rest of the spectrum, though they are not absolutely black, it is merely a matter of contrast. This is the explanation of the Fraunhofer lines in the solar spectrum and of the dark lines in the spectra of the stars, and it is by the analysis of such spectra that we can tell of what elements the cool atmosphere surrounding a star is composed. The light from the stars carries its own message, and what a tale it can unfold when we learn to read the language in which it is written!

165. Full Radiation or Black Body Radiation.—We have seen the unique character of the radiation in a uniform temperature enclosure and we must now consider another aspect of it. Let us suppose that a body which is a complete absorber for every wave-length is placed in the enclosure, such a body is called a **black body**, since it would appear black by whatever light it was viewed. It does not affect the radiation stream in the enclosure and so it must restore to it by emission what it takes from it by absorption. But it absorbs the whole stream completely and so it emits a radiation stream identical in both quantity and quality with that in the enclosure. So the radiation in a uniform temperature enclosure is sometimes called **black-body radiation**, since it is identical with that emitted by a black body. Moreover, since a black body has the maximum absorbing power for every wave-length, by Kirchhoff's law its emission is the greatest possible for every wave-length at any given temperature. So the radiation it emits and that inside in a uniform temperature enclosure is also known as **full radiation**.

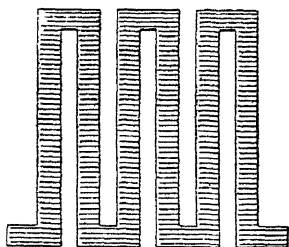
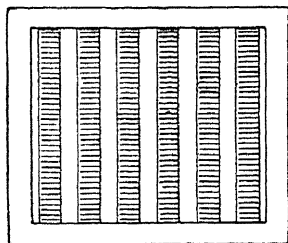
All this is very interesting, but quite useless if we cannot obtain this full radiation for practical investigation. It is obvious that we cannot carry on experimental investigations inside a uniform temperature enclosure at any appreciable temperature, but we can reproduce the radiation in such an enclosure if we can only produce a black body. We can get as near to this as we like by taking an enclosure lampblackened on the inside and making a small hole in it. The *hole itself*, not the walls of the enclosure, is to be regarded as the surface of the black body. It can be seen that almost all the radiation entering the hole will be absorbed by the lampblackened interior; most of the small

amount which is diffusely reflected will strike another part of the interior and only a very small fraction will emerge from the hole again. This fraction can be made as small as we please by making the hole small enough. If such an enclosure is heated to a uniform temperature, the radiation which issues from the small hole is as nearly as we like identical with full radiation. It must be emphasised that in a practical investigation care must be taken that only radiation issuing from the hole must be allowed to reach the measuring instrument, which must be screened from any which may be emitted from the walls of the enclosure.

166. The Measurement of Radiation.—In order to determine the relation between full radiation and the temperature of the body emitting it, we require instruments to measure radiation. Since radiation is merely a form of energy, which can easily be converted into heat by causing it to fall on any body which can absorb it, the problem really resolves itself into the construction of a suitable instrument for measuring a small quantity of heat, that is, a small rise in temperature. The blackened bulb of an ordinary liquid thermometer was soon replaced by a differential air thermometer depending on the expansion of air when heated. This, in turn, was superseded by the thermopile, which depends on the E M F produced in a circuit consisting of two different substances when the junctions are at different temperatures. This instrument has been brought to the highest degree of sensitiveness by Boys in his radio-micrometer, which is a combination of a thermo-couple and a very sensitive galvanometer. All of these instruments are rather for the detection of radiation and a rough measurement of it than a precise measure of the number of ergs of radiation falling on the instrument per second. We shall now describe two instruments, one, the **Lummer-Kurlbaum bolometer**, whose readings are proportional to this quantity, and another which measures it absolutely.

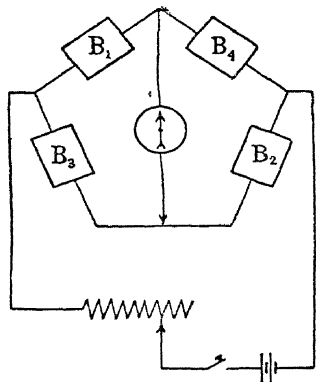
167. The Lummer - Kurlbaum Bolometer.—The Lummer-Kurlbaum bolometer, which is an improvement on the original instrument due to Langley, depends on the increase of the resistance of a piece of platinum when heated

It consists of four, identical, very thin strips of platinum of the form shown in Fig 107*a* and suitably mounted in slate frames as shown in Fig 107*b*. The strips are only 0.0005

FIG 107*a*FIG 107*b*.

mm. thick so as to have the minimum thermal capacity for a given surface area, this causes the bolometer to reach its equilibrium temperature in the shortest possible time when exposed to radiation. To increase the sensitivity the strips are lampblacked so as to make them absorb as much as possible of the radiation falling on them.

One strip B_2 is mounted behind another B_1 so that its lengths of platinum cover the spaces of the other strip, thus ensuring that no radiation is lost. These two strips are mounted in opposite arms of a Wheatstone bridge (Fig 107*c*), the remaining two arms being completed by the other two strips B_3 and B_4 , which are mounted in a case to shield them from radiation. By this arrangement twice as much radiation falls on the bolometer as with a single strip of platinum, and by the arrangement of the strips in the Wheatstone bridge the effect of the change in resistance is doubled. The bridge is balanced by the sliding contact with all the four strips shielded from

FIG 107*c*

radiation and it is then found that, if B_1 and B_2 are exposed to the stream of radiation under test, the deflection of the galvanometer due to the upsetting of the balance of the bridge is proportional to the amount of radiation falling on the bolometer in unit time. This is solely due to the fact that the rise in temperature of the strips and the disturbance of the balance are both small, and so the relation between the quantities concerned is approximately linear for such a small range of variation.

This instrument is suitable for measuring the amount of radiation in the whole of the spectrum emitted by a body, if we wish to measure the amount confined to a narrow region of wave-lengths, we use a line bolometer, which consists essentially of one narrow strip of blackened platinum contained in a Wheatstone bridge arrangement. We form a spectrum of the black body radiation by a reflection grating and place the line bolometer in it, when it measures the amount of radiation emitted per second lying between those wave-lengths which fall on the bolometer.

168. An Absolute Bolometer.—We shall describe the modification of the Ångström pyrheliometer due to Coblenz as our instrument for measuring the number of ergs of radiation falling on it per second. It consists of two blackened strips of platinum suitably mounted, so that one can be exposed to the stream of radiation to be measured, while the other is shielded from it but can have an electric current passed through it. One junction of a thermo-couple is attached to the back of one strip and the other to the other. Both strips are shielded from radiation to start with, and no current is registered on the galvanometer connected to the thermo-couple. One strip is then exposed to the radiation under test and such a current is passed through the other as to keep the deflection of the galvanometer zero. This means that the temperature of the two strips is remaining the same, and therefore that the electric current is supplying energy to the one strip at the same rate as radiation is falling on the other. But we can easily measure the electrical energy supplied to the strip by measuring the current in amperes passing through it and the P D in volts across it, their product giving the amount of radiation in joules falling on the instrument per second.

169. Relation between the Quantity and Quality of Full Radiation and Temperature.—The law which is found to relate the quantity of full radiation and temperature was arrived at by a consideration of the results of an elaborate set of experiments by Dulong and Petit on the rate of cooling of a hot body. They found in the first place that their results were consistent with an expression of the form

$$V = k\{f(\theta) - f(\theta_0)\},$$

where V is the rate of loss of temperature of the hot body when it is at a temperature $\theta^\circ \text{C}$ in an enclosure at a temperature $\theta_0^\circ \text{C}$. It may be pointed out that this supports Prévost's theory of exchanges, for it tacitly assumes that the observed loss of heat is really the difference in the heat radiated by the hot body and that absorbed from its surroundings. If the first view of radiation we took in this chapter were true, it should be possible to express the rate of cooling of a hot body as a function of its excess temperature over that of the surroundings, which has not been done for large values of the excess temperature, such as 100°C .

Dulong and Petit proposed an exponential form for $f(\theta)$ and this fitted their results quite well, but a Russian, Stefan, on examining their results, found that they accorded even better with the equation

$$V = k(T^4 - T_0^4),$$

where T is the absolute temperature of the hot body in an enclosure at absolute temperature T_0 . This means that the amount of energy E in ergs radiated per sq. cm. per second by a black body at absolute temperature T is given by

$$E = \sigma T^4, \quad . \quad . \quad (92)$$

where σ is a constant. This is called **Stefan's law**, but since Dulong and Petit did not use a black body in their work, further experiments with such a body are required both to see if the law is true in its case and also to determine Stefan's constant, σ .

An accurate series of experiments for this purpose has recently been carried out by Coblentz using an electrically heated black body, whose temperature was measured by

a thermo-couple. The amount of radiation emitted by the black body was measured by the modified pyrheliometer described in the previous article. This measures the amount of radiation falling on the pyrheliometer in one second, and from its area, that of the black body, and their distance apart, the amount of radiation emitted by the black body per sq cm per second can be calculated. The experiment consists essentially in measuring the difference in the amount of radiation absorbed by the pyrheliometer when it is receiving radiation from the black body at temperature T_1 and when the hole in the enclosure constituting the black body is closed by a water-cooled shutter at temperature T_2 . From this, Q , the difference in the energy radiated per sq cm per second by the black body and the water-cooled shutter can be calculated. Then, if Stefan's law is true for a black body,

$$Q = \sigma(T_1^4 - T_2^4)$$

Coblentz found that this equation was obeyed for temperatures up to 1600°C and therefore Stefan's law is true for that range of temperature. His value for σ was 5.72×10^{-5} ergs per sq cm per second per degree 4 .

We may mention, in conclusion, that Stefan's law has been derived theoretically by Boltzmann. He was able to obtain a relation between the energy density of full radiation and its temperature by applying the second law of thermodynamics to a heat engine in which radiation was the working substance. It can act as such because it can carry energy and can do external work by virtue of the pressure it exerts on any surface which reflects or absorbs it. Boltzmann found that the energy density of full radiation is proportional to the fourth power of the absolute temperature of the enclosure. It is a simple matter to show that this leads to Stefan's law.

In a previous article (Art 164) we have defined $e_\lambda d\lambda$ as the amount of radiation lying between wave-lengths λ and $\lambda + d\lambda$ emitted per sq cm per second by a body at a temperature T . Our next problem is to investigate how e_λ for a black body depends on λ and on T , in other words, to see how the energy of full radiation is distributed among the different wave-lengths at various temperatures. Very

briefly, this is done by forming a spectrum of the radiation of a black body at a given temperature with a reflection grating and measuring the distribution of energy with a line bolometer. The results obtained at various temperatures are shown in Fig 108 and from these curves two laws can be induced. They are

$$\lambda_m T = \text{constant}, \quad . \quad . \quad . \quad (93)$$

where λ_m is the wave-length at which e_λ is a maximum at temperature T . This is known as **Wien's law**, and means that as the temperature increases, the bulk of the radiation emitted tends to be associated with shorter wave-lengths. It accounts for the fact that as the temperature of a body is raised, it emits first of all only infra-red radiation, then red light, then yellow light, and finally white light. If we could attain even higher temperatures in the laboratory, we could make bodies "blue hot," as is actually observed with some of the stars. The other law states

$$(e_\lambda)_{\max} = \text{constant } T^5 \quad (94)$$

Following up Boltzmann's work, Wien has derived both of these laws theoretically by means

of the second law of thermodynamics, but it is not possible to obtain a mathematical expression relating e_λ , λ , and T in this way. This can only be done if some assumption is made as to the actual mechanism of emission and absorption of radiation. Some attempts have been made in this direction, and they will be touched on in the Conclusion.

170. The Measurement of Temperature by Radiation.—It is evident that we can measure the temperature of a body by an examination of the radiation stream which it emits. Two ways are open to us, we can either use

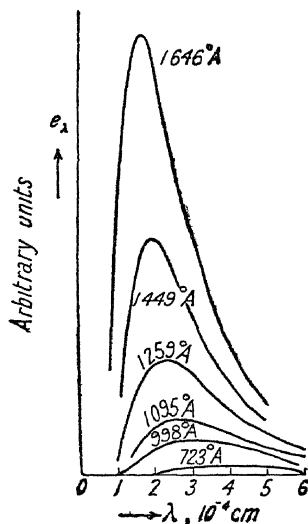


FIG 108

Stefan's law or one of the two laws expressed in equations (93) and (94). The superiority of these methods over any which we have so far described is that there is no limit to the temperature which can be measured by the radiation method, since the measuring instruments are not in contact with the hot body. In all other types of thermometer the bulb must be placed in contact with the hot body and so it cannot measure temperatures above the melting-point of the material of the bulb. In practice this imposes an upper limit of about 1600°C . The radiation method has one disadvantage. Since it uses one of the equations (92), (93), or (94), it tacitly assumes that the body whose temperature is being measured is a black body. This is by no means necessarily the case, and when it is not the measured temperature will be too low. This is because a black body is a full radiator and either the total quantity of radiation it emits or that of any particular wave-length is greater than that sent out by the given body when they are at the same temperature. The radiation method measures what is called the **black body temperature**, which is a lower limit to the actual temperature of the body.

171. Féry's Total Radiation Pyrometer.—This instrument measures the temperature of a body by means of

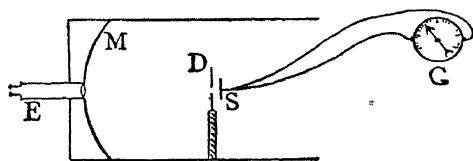


FIG 109.

the total radiation which it emits and is shown diagrammatically in Fig 109. The radiation from the hot body is focussed by the concave mirror *M* on to the diaphragm *D*.

The eyepiece *E* is to enable this to be done by a device, the details of which are irrelevant. The radiation then falls on the blackened strip *S*, to the back of which one junction of a thermo-couple is attached. The radiation heats up this strip and so produces a current which deflects the galvanometer *G*. Arrangements must be made to use the pyrometer at such a distance from the body that the image of it completely fills the hole in the diaphragm. Then the reading of the galvanometer is inde-

pendent of the precise distance between the pyrometer and the body. This is because the reading depends on the brightness, or amount of radiation per unit area, of the image if it is larger than the hole. The brightness is independent of distance, since, if the distance is doubled, the amount of radiation falling on the mirror M is divided by four, but so is the area of the image.

In practice it is found that the deflection of the galvanometer is not proportional to the fourth power of the absolute temperature of the body and so it has to be calibrated. This is done by sighting the pyrometer on a black body, whose temperature can be measured by a standard thermo-couple. The black body can then be raised to various known temperatures and the corresponding deflection of the galvanometer can be read. In this way a calibration curve of galvanometer deflection and temperature can be drawn up or the galvanometer can be calibrated directly in degrees.

172. The Disappearing Filament Pyrometer.—This makes use of the radiation confined to a small range



FIG 110

of wave-lengths and is illustrated diagrammatically in Fig 110. The body B whose temperature is to be measured is focussed by the lens L on to a filament F, whose temperature can be adjusted to any desired value by passing a suitable electric current through it, which is measured with an ammeter. The filament and the image of the body are viewed through a piece of special glass R with the eyepiece E. The glass only allows a narrow range of wave-lengths in the red to pass through it. The current through the filament is adjusted until the filament disappears against the background formed by the image of the body under test. This means that the brightness of the red light emitted by the filament

is the same as that emitted by the body. If the brightness, or energy emitted per square centimetre per second, is the same in the two cases, then their temperature is the same. The instrument is calibrated by sighting it on a black body, whose temperature can be measured with a standard thermo-couple, the ammeter which measures the filament current being calibrated directly in degrees. We may notice, in conclusion, that the method of direct calibration restricts the range of these thermometers to that of the gas thermometer, thermo-couple, and so on. But they are preferable to them in industry, since they are direct reading, quicker, easier to use, and do not need to be in contact with the body whose temperature is being measured.

173. The Measurement of the Temperature of the Sun.—The above two radiation thermometers can only be used up to the same temperature as ordinary thermometers, and we must now describe how temperatures above this range are measured. Our method must give temperature on the work scale. How can this be done when we are going outside the range of the gas thermometer, which has so far been our only method of getting at a temperature on the work scale? First of all, Stefan's law and those represented by equations (93) and (94) are not only verified by experiment for the range of the gas thermometer, but theory suggests that they are true for any range of temperature. The law we have used in establishing this is the second law of thermodynamics, which, we have seen, is the one law in physics on which we can place the most reliance. So we shall be safe in using these laws as our basis. Furthermore, as a confirmation of this, Lummer and Pringsheim undertook a series of experiments in which they measured the temperature of a specially constructed black body at about 2300° A. by all the three methods; that is, using Stefan's law, the law relating the wave-length corresponding to the maximum emission, and the one relating the actual maximum energy of emission and temperature. The results obtained by each method agreed with one another to within the limits of experimental error, showing that the use of any of these three laws is justified outside the range for which they have been experimentally verified.

We shall illustrate the method adopted by describing the classic case of the measurement of the temperature of the sun. First of all the **solar constant** is measured. This is the amount of radiation which would fall in 1 minute on a surface of 1 sq cm in area placed normal to the sun's rays at the distance of the surface of the earth from the sun outside the earth's atmosphere. This quantity is measured by an absolute instrument such as that described in Art 168, a correction being made for the absorption of the atmosphere. The most reliable results so far obtained lie between 2 and 2.5 calories per sq cm per minute. Taking 2.3 as our value, we have the total amount of energy radiated by the sun per minute $= 2.3 \times 4\pi \times (93,000,000 \times 5280 \times 12 \times 2.54)^2$ calories. If we take the radius of the sun as 430,000 miles, we have the amount of energy radiated per sq cm per minute by the sun

$$= \frac{2.3 \times 4\pi \times (93,000,000 \times 5280 \times 12 \times 2.54)^2}{4\pi \times (430,000 \times 5280 \times 12 \times 2.54)^2}$$

$$= 1.08 \times 10^5 \text{ calories}$$

From equation (92), assuming Stefan's constant to be 1.37×10^{-12} calories per sq cm per second, we have

$$1.08 \times 10^5 = 60 \times 1.37 \times 10^{-12} \times T^4$$

where T = the black-body temperature of the sun in °A.
 $\therefore T = 6000^\circ \text{A}$

This method is applicable both to the stars and terrestrial bodies at very high temperature above the range of ordinary thermometers

EXAMPLES ON CHAPTER XV

1 What are the principal points of resemblance and difference between radiant heat and visible light? How would you demonstrate them experimentally? (*O and C*)

2 Give the various means whereby heat may be transmitted and show how all these are reduced to a minimum in a thermos flask made with a long tapering cork (*Camb Schol*)

3 Write a short essay on the infra-red region of the spectrum (*Camb Schol*)

4 How would you show that a large amount of the energy radiated by a gas burner consists of non-luminous heat radiation? How would you measure the amount of absorption by a sheet of glass? (*Oxford Schol*)

5 Discuss the evidence, both experimental and theoretical, in favour of the view that "good emitters are good absorbers"

6 Give an account of some outstanding examples of the fact that a body which emits radiation well is also a good absorber

7 Show that the radiation in a uniform temperature enclosure depends only on the temperature of the enclosure and not on the material of which it is made or on the presence of any other bodies in the enclosure. Why is such radiation called "full radiation" and why is it the same as "black body radiation"?

8 Describe a sensitive instrument for the detection and measurement of radiant heat

Explain how the reading on such an instrument depends on the area, distance, inclination and temperature of a black surface, the radiation from this being received by the receiving surface in a direction normal to that surface (*Tripes, Part 1*)

9 Give a short account of the methods and results of experiments which have been made to investigate the variation of the rate of radiation of heat with temperature (*Camb Schol*)

10 What is meant by "black body radiation" at a given temperature? Describe some method by which it may be investigated (*Camb Schol*)

11 What is meant by the "quality" of the radiation emitted by a body? Give a very brief account of the way in which the quality of the radiation emitted by a black body and its variation with temperature have been investigated. Draw graphs to illustrate the results which have been obtained and state the laws which have been induced from them

12 If the total radiation from unit area of a body be given by $\sigma\theta^4$ where θ is the absolute temperature and σ has the value 5.3×10^{-8} in C.G.S. units, calculate the temperature of the Earth, assuming that it absorbs half the energy falling on it from the Sun (Radius of Sun 7×10^{10} cm, radius of Earth 6.3×10^8 cm, mean radius of orbit of the Earth 1.5×10^{13} cm, temperature of Sun's surface 6000° Abs) (*Oxford Schol*)

13 State Stefan's law of radiation, pointing out the type of radiator to which it applies. Indicate briefly (1) how such a radiator is realised in the laboratory, (2) how it is used to extend the temperature scale above 1600° C (*N.U.I.B.*)

14 A silver disc fitted with a device for indicating its temperature is suspended in front of a gas fire. The side facing the fire is blackened and the reverse side is highly polished.

(a) Draw a graph showing how you would expect its temperature to change from the moment at which it is placed in this position.

(b) Show how you would determine the number of calories which it receives per second from the fire. (*N U J B*)

15 Give an account of radiation methods of measuring high temperatures. (*Tripos*, Part 1)

16 Calculate the temperature attained by the glass bulb of a 100 watt electric lamp in a vacuum, if the bulb is a sphere of 5 cm radius and the filament may be treated as a point source. You may assume that the temperature of the surroundings is 15°C , the glass absorbs 75 per cent of the radiation falling on it, that it emits three-quarters as well as a full radiator, and you may neglect the radiation emitted from the inner surface of the glass bulb. Does your answer depend on the value of the absorptive and emissive power of the glass?

Explain carefully how the temperature attained by the glass bulb will alter if the lamp is transferred from a vacuum to the atmosphere.

Conclusion.—We have now come to the end of our journey and it is natural to turn back and survey the ground we have covered, that we may the better appraise the worth of the new territory we have won. At the outset of the journey we stated that it was our aim to fit the facts into a rational scheme and it has been the ideal of Victorian physics to interpret this as an attempt to explain all the phenomena of physics in terms of mechanics. Lord Kelvin was perhaps the most famous exponent of this view, and he believed that all the phenomena of heat, light, sound, and electricity and magnetism would be ultimately explicable in terms of mechanics applied to the ultimate particles of matter. He went even further than this and asserted that no phenomenon was ever really satisfactorily explained unless a mechanical model of it had been made.

What have we achieved in the light of this point of view? We have succeeded in obtaining a qualitative explanation of the thermal behaviour of solids, liquids,

and gases on the kinetic theory of matter, which is based on the application of mechanics to the molecules of matter. Further, we have obtained a complete mathematical explanation of the properties of the ideal gas working on the same lines, and it has been possible to extend the theory to actual gases and to give a picture of the transition from the liquid to the gaseous state. Of these various extensions we have only described the one due to Van der Waals, since it achieves more for a given number of assumptions than the other attempts. This illustrates yet another aspect of science, namely, the æsthetic element. Some of the other equations of state fit the facts even more closely than Van der Waals' equation does, yet many people place very little reliance on such theories. The reason is that they contain too many assumptions, some of which seem to be designed to produce the right result rather than to follow from the nature of matter itself. To put it another way, these theories give no intellectual satisfaction, they make no æsthetic appeal, and where two theories explain the facts equally well, this is the decisive criterion. There is much to be said for the view that a given set of facts can be explained by quite a number of theories and that therefore the æsthetic element in science is really the most important one.

The other great generalisation which has emerged from our study of heat is the Second Law of Thermodynamics. This arose from the study of heat engines and has found the most widespread applications in all branches of science, pure and applied, and has finally made its way into the realm of philosophy and theology. This is on account of the fact that it predicts the ultimate stagnation of the physical universe, a state in which literally nothing can happen. But perhaps an even greater reason for its importance is the fact that it is one of the laws of physics, the probability of whose being broken can be calculated, and the chances turn out to be so minute that they are not worth reckoning on. One final word may be said, it may be necessary to revise this law in the light of new facts or new theories based on such facts, but everything appears to be against this at the moment.

Having reviewed those generalisations which have been successful, we must now turn to the failures. We do so, not with any sense of despair, but in the hope that the ultimate outcome will be new and even more interesting knowledge, as has so often been the case in the past. We may mention two cases of this. In the first place, it was the failure in the agreement of the densities of atmospheric and chemically prepared nitrogen which led Rayleigh and Ramsay to the discovery of the rare gases of the atmosphere, secondly, it was the failure to account along orthodox methods for the line of atomic weight 22 which appeared in the positive ray analysis of neon, which led Aston to the discovery of isotopes.

We shall now discuss two failures in the realm of heat of the attempt to explain the facts in terms of classical mechanics. The first concerns the atomic heat of solid elements and the molecular heat of gases. In each case the kinetic theory leads to the view that the molecular heat has a certain numerical value and is independent of temperature. This fits the facts quite well at ordinary and higher temperatures, but it breaks down completely for low temperatures. We have already seen in Art. 24 in the case of solid elements that experiment shows that the atomic heat tends to zero as the absolute zero is approached and the same is true of gases. We saw in Art. 23 that Einstein had suggested a new theory, called the quantum theory, which gave a general explanation of the facts. The feature of this theory is the discontinuity of energy and so it can be seen that it cuts right across the classical theory of mechanics. For this reason many physicists found themselves unable to accept Einstein's theory and took the view that the classical mechanics had failed to account for the facts of specific heat, not because the laws of classical mechanics were wrong, but because the assumptions as to the nature of the heat energy were untrue.

The second discrepancy between fact and theory is in the distribution of the energy in the spectrum of a black body. All attempts to explain this on the classical mechanics lead to the equation

$$E_{\lambda} = 8\pi kT\lambda^{-4},$$

where the symbols have their usual meanings. The interpretation of this equation is that the amount of energy situated in the short wave-lengths is infinite, which is manifestly contrary to experience. In fact, experiment shows that the total amount of energy distributed among all wave-lengths is considerably less than the heat energy of the black body. Planck first put forward the quantum theory to explain this discrepancy and his results are in good agreement with experiment, but his theory was not accepted at first since it is contrary to the classical mechanics. But in 1912 the French mathematician, Poincaré, showed in a brilliant piece of analysis that the facts of black body radiation could never be explained on any theory in which energy was continuous, and that some such discontinuity as postulated in the quantum theory was essential.

Poincaré's work marks the turning-point in the controversy between the supporters of the classical and quantum theories, and since then attempts have been and are still being made to find a quantum mechanics, which will explain the facts of specific heats and black body radiation, and at the same time reduce to the classical mechanics in all ordinary phenomena. The mistake the supporters of the classical mechanics made was to suppose that it would not only fit the facts in the macroscopic world, for which it was originally designed, but also those in the world of atoms. It turns out that this is not the case, and the assumption that it would be so was an extrapolation. It is the same thing as assuming that, because a certain graph is a straight line over a certain region which has been investigated experimentally, it will continue to be so over a wider region. Such an assumption is called an extrapolation and is always subject to revision in the light of experiment.

The present state of affairs illustrates yet another aspect of science, with which we may conclude this book. It is that science is a series of approximations to the truth, at no stage do we claim to have reached finality; any theory is liable to revision in the light of new facts. In this book we have completed one approximation in the case of heat and have led the reader to the stage at which it becomes

apparent that it is only an approximation. And, on this note, we must now take leave of him and refer him to more advanced books on the subject for a full account of the new mechanics. This is both the joy and inspiration of science, that there appears to be no end to new knowledge with its interest. Each advance yields a more far-reaching and interesting picture of the physical world, while at the same time opening up fresh views in the shape of new problems awaiting solution.

ANSWERS TO NUMERICAL EXAMPLES

CHAPTER I

3. 10.2°C , 68.3°C .; 0.8°C 7. 44.2°C 13. 422°C , 267°C , 274.3°C 19. 600 cm , 994 ohms , 2.5°C 22. 51°C , 40°C 23. 17°C , 30.4°C , 40°C , 80°C

CHAPTER II

2. 19.4°C 3. -185°C 4. 9.35 hp , $13.1^{\circ}\text{C per min}$
5. 16°C , 43°C 6. 16.9 7. 8.22 min 10. $0.45\text{ cal per grm per }^{\circ}\text{C}$ 11. $0.77\text{ cal per grm per }^{\circ}\text{C}$ 13. 14.0 cal per grm 14. 80 cal per grm 17. 100.5 cal per grm 18. 15.14°C , 15.57°C 21. $3.39\text{ cal per grm per }^{\circ}\text{C}$

CHAPTER III

3. 0.180 in 4. 75.351 cm , 24.996 cm 5. 67.4°C 6. 500°C 7. 53.6 sec 9. 4007.924 sq cm , 4007.920 sq cm , 0.0001 per cent 10. $475 \times 10^{-7}\text{ per degree}$

CHAPTER IV

1. 4.366 grm 2. 106.260 cc , 106.360 cc , 0.1 per cent
3. 35.89 grm 4. 75.6°C 5. 69.3°C 6. $0.0000033\text{ per }^{\circ}\text{C}$, $0.000539\text{ per }^{\circ}\text{C}$ 9. $0.000916\text{ per }^{\circ}\text{C}$ 12. 751.5 mm
13. 75.207 cm 14. 75.33 cm

CHAPTER V

2. 32.2 cc 3. 6.9 cc 4. $0.078\text{ grm per litre}$ 5. 14.1 cm 6. 538°C 7. $\frac{1}{288^{\circ}\text{F}}$ per $^{\circ}\text{C}$ at 0°C 8. 1.55
9. 0.993 12. 77.5 cm 13. $2.065 \times 10^6\text{ ergs per grm per }^{\circ}\text{C}$

CHAPTER VI

13. Difference in boiling-point is 0.067°C 14. 96.6°C .

CHAPTER VII

3. Decrease the volume of the air to 20 c.c. 4. 2.04 km
 9. 38 i per cent 12. 0.154 grm, $\frac{1}{66}$

CHAPTER VIII

3. 0.75 h.p. 5. 93.4 grm 8. 0.99 cal per grm per °C
 9. 2.54×10^7 ergs per calorie 11. 4.165 joules per calorie
 12. 59.5 calories 13. 582 B.Th.U. 14. 4.19×10^7 ergs
 per calorie 15. 0.117° C 16. 156° C

CHAPTER IX

5. 1.84×10^5 cm per sec, 2.15×10^5 cm per sec,
 $\frac{2.60 \times 10^5}{\sqrt{m}}$ cm per sec, $\frac{3.02 \times 10^5}{\sqrt{m}}$ cm per sec 7.
 5.11×10^4 cm per sec 8. 3.38×10^{10} cm² per sec.² 9.
 1.84×10^5 cm per sec

CHAPTER X

13. 1.50° C

CHAPTER XII

4. -54.8° C 5. 13.4° C, 4.87 grm 7. -24.6° C.
 8. -47.9° C 9. 185.6° C 10. If p_0 is the initial pressure,
 $\frac{2}{3}p_0$, 0.564 p_0 , -42.2° C

CHAPTER XIII

8. 0.041 h.p. 13. -0.0074° C 15. 0.36° C.

CHAPTER XIV

2. 0.392 cm per hour, 19 hours 13. 6870 cal. 14.
 2050 cal 15. 102.4° C 16. 2.61 cm 18. 151.24° C,
 1.75 amp 19. 48.9° C, 135.6° C 20. $\theta = 100(1 - e^{-\beta l})$,
 where θ is the temperature l cm from the entrance to the
 tube and $\beta = \frac{2\pi\kappa}{y \log \frac{s}{r}}$ 21. 0.198 cal, 0.70 cal per sq. cm.
 per sec per unit temp. gradient 22. 1.13×10^{-4} C.G.S.
 units 23. 308 min 24. 994,000 cal 27. 4.34 cal per
 sec

CHAPTER XV

12. 290° A 16. 227° C.

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